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The Equatorial Longitude Effect in Cosmic Rays

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(Received December 3, 1934)

AT the meeting of the National Academy of Sciences and the American Physical Society, held in Washington, D. C., April 24th and April 27th, respectively, we made our first public presentation of the evidence for the existence of a theretofore unsuspected cosmic-ray effect which we called "The Longitude Effect." This evidence consisted in the projection and discussion of Figs. 1 and 2, again reproduced herewith. In the first of these were collected the readings of our self-recording, vibration-free, Neher electroscope, when taken inside its 10 cm lead shield, on four separate passages made in the interval November 1932 to January 1934, between Los Angeles and the western coast of South America.

The curve shows an equatorial dip of 7 percent in terms of the mean Los Angeles reading of these electroscopes. It was because this equatorial dip was only about half that reported by Clay on the other side of the world, and by some other observers on this side, that we took extreme precautions to check and recheck it, and to withhold *final* publication until this had been done with the utmost care.

In our effort to obtain accuracy, we had the great good fortune of being able to place one of our self-recording electroscopes, inside its 10 cm lead shield, on Captain G. Allan Hancock's yacht, the Velero III, which was going on a three month's cruise to Guayaquil and the islands off the coast of Equador. It required no attention save to have the clock wound once in two days. Because of the fact that Captain Hancock stopped three times for 9 and 10 days at a time in three different ports in the equatorial belt (see the three adjacent circles Fig. 1), and also for 10 days in Los Angeles harbor (uppermost circle), the mean intensity in each one of these points, as well as in intermediate latitudes where his three day stops were made, was determined with much greater accuracy than had theretofore been attained.

In Fig. 1 are also found the readings obtained on the other trips, and they are all seen to be in good agreement, but the findings on the Velero III were given especial weight in the fixing of the precise position of the curve of Fig. 1. Fig. 3 shows a bit of the developed film. The rate of discharge during an hour's run is given by the slope of each diagonal line of this film. The mean of 24 of these slopes gives the mean intensity for that day, and the mean of $24\times 7=168$ slopes the mean for a week.

In Fig. 2 we showed the readings of a precisely similar electroscope when placed, in August 1933, in the room of Captain Cullen of the Dollar Line ship, President Garfield, and carried on a voyage around the world starting from Los Angeles. Three months later after the return of the ship to Los Angeles, following her world cruise to Honolulu, Japan, the China coast, Singapore, Ceylon, the Red Sea, the Mediterranean, the Atlantic to New York, and then back to Los Angeles via Panama, we removed and developed the film in the Norman Bridge Laboratory and found a remarkably good record until New York was reached. The results of this record were incorporated into Fig. 2, which shows a 12 percent

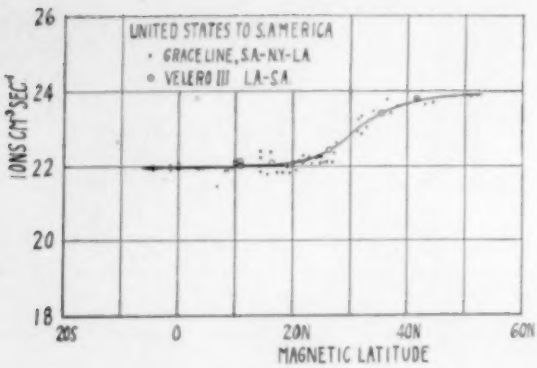

FIG. 1.

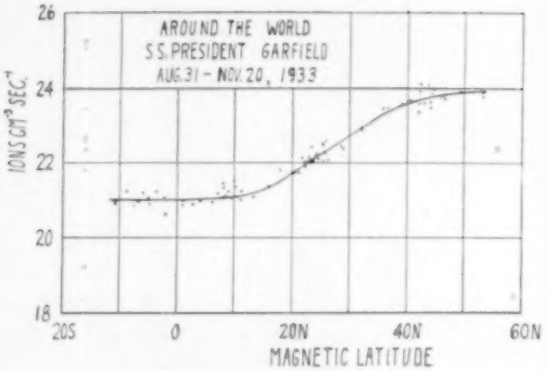

FIG. 2.

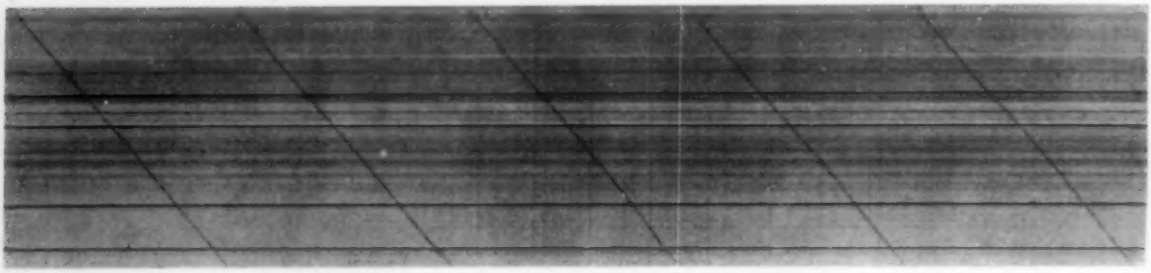

FIG. 3. Neher electroscope hourly discharge record.

dip in going into the equatorial belt on the Asiatic side of the earth instead of the 7 percent dip shown in Fig. 1 on the South American side.

This "longitude effect" was thus brought sharply to light with the measurement of this film which was completed January 10, 1934. In presenting these results to the Physics Club in Pasadena, immediately thereafter, and also to the Physical Society in April, we pointed out that the value of the horizontal component of the earth's magnetic field is 0.4 gauss in the Singapore area and but 0.3 gauss in the equatorial belt off South America, a fact which prompted our suggestion that the dissymmetry in the earth's magnetic field as manifested at the earth's surface is also reflected in the regions thousands of kilometers above the surface where the incoming electrons must in the main receive their deflections. At any rate these observations put into our hands, for the first time, a method of studying the shape of the earth's magnetic field far above the earth's surface, instead of merely at the surface as heretofore.[1]

Since last April when the foregoing results were reported both to the American Physical Society and the National Academy of Sciences, and publicly and critically discussed with the physicists who are interested in cosmic-ray surveys, we have, in June 1934, placed one shielded and one unshielded, Neher electroscope, in the room of First Officer Graham, just back of the bridge of the S. S. Monterey of the Matson Line, and got an excellent record both going and coming between Los Angeles and Sidney, Australia, in the case of the shielded electroscope, and a good record in the unshielded one on the way down. Further, we have sent another unshielded electroscope on a voyage between Los Angeles and Mollendo.

All of the results thus far taken with our electroscopes shielded with 10 cm of lead, are graphed together in Fig. 4 and those taken with unshielded electroscopes in Fig. 5. It will be seen too that the mean of 10 days of readings in Los Angeles harbor is nearly a percent lower than

[1] Professor Clay informs us by letter that he made the discovery of the longitude effect independently as a result of an expedition between Amsterdam and Batavia, via Suez going, via Capetown returning, made between September 1933, and January 1934, the results of which he commented upon very briefly in Physica, March 1934, p. 363, and more at length under the designation "Longitude Effect" in Physica, August 1934, p. 829.

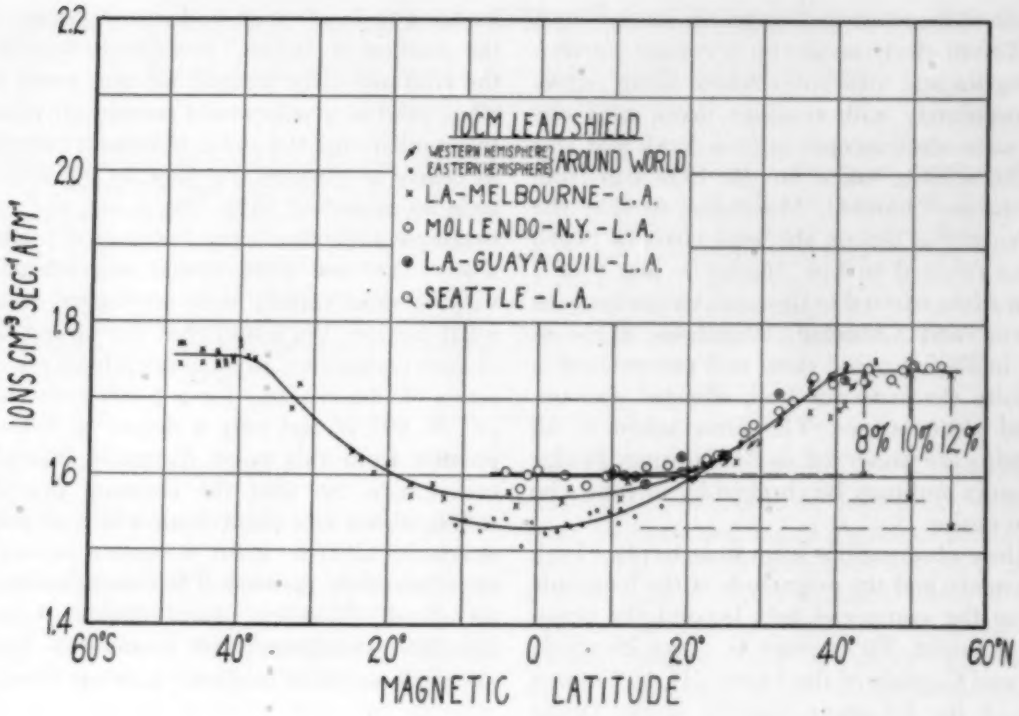
10CM LEAD SHIELD
WESTERN HEMISPHERE
EASTERN HEMISPHERE
AROUND WORLD
L.A.-MELBOURNE-L.A.
MOLLENDO-N.Y.-L.A.
L.A.-GUAYAQUIL-L.A.
SEATTLE-L.A.
8% 10% 12%
IONS CM⁻³ SEC.⁻¹ ATM⁻¹
2.2
2.0
1.8
1.6
1.4
60°S
40°
20°
0
20°
40°
60°N
MAGNETIC LATITUDE

FIG. 4.

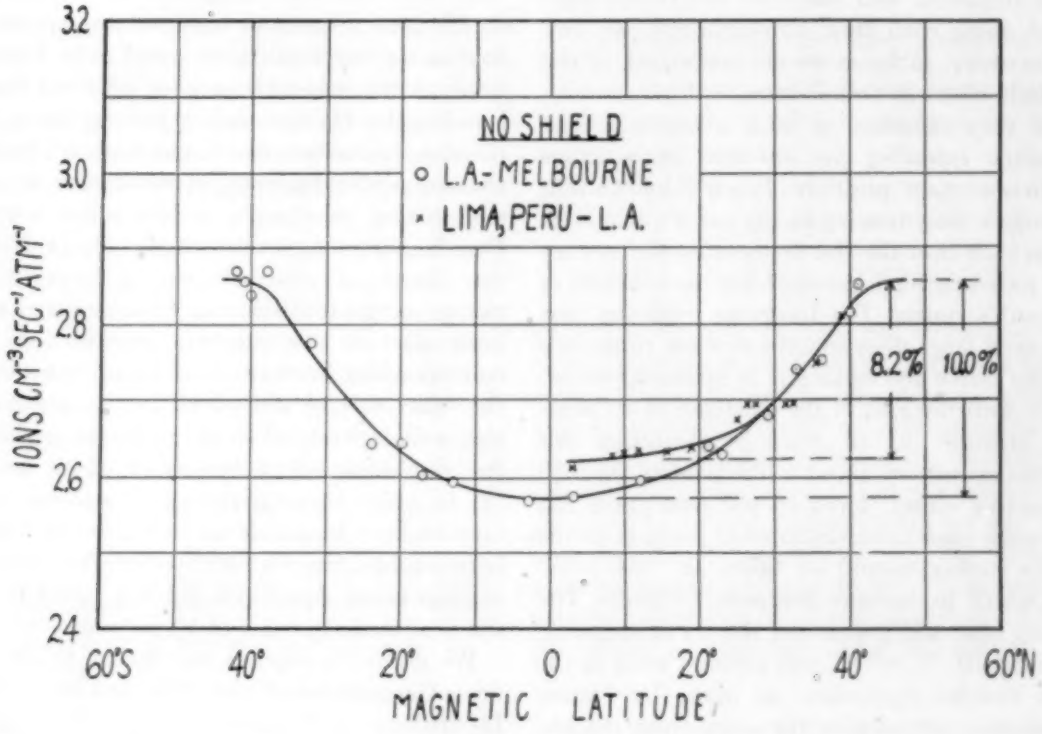
NO SHIELD
L.A.-MELBOURNE
LIMA, PERU-L.A.
8.2% 10.0%
IONS CM⁻³ SEC⁻¹ ATM⁻¹
3.2
3.0
2.8
2.6
2.4
60°S
40°
20°
0
20°
40°
60°N
MAGNETIC LATITUDE

FIG. 5.

the mean of the readings that we have taken with two different electroscopes on a voyage between Los Angeles and Vancouver which mean agrees quite accurately with readings taken with one of the same electroscopes in New York and also with the reading taken on the 1930 trip from Pasadena to Churchill, Manitoba; so that the total equatorial dip on the west coast of South America referred to Los Angeles is just over 7 percent while referred to the mean values between Pasadena and Churchill, Manitoba, it is as shown in Figs. 4 and 5 close to 8 percent and is essentially the same for both shielded and unshielded electroscopes. The films taken in all these trips are preserved in the Norman Bridge Laboratory and may be checked by anyone who may so desire.

All these observations seem to us to place both the existence and the magnitude of the longitude effect in the equatorial belt beyond the possibility of doubt. To Captain G. Allan Hancock, owner and Captain of the Velero III, to Captain Cullen of the President Garfield of the Dollar Line, and to First Officer Graham of the Monterey of the Matson Line, all of whom kept our log as requested and saw that our clocks were wound along with their chronometers, we owe the discovery, so far as we are concerned, of the longitude effect in cosmic rays.

The very existence of such a magnetic dissymmetry *extending far out into space* raises certain important questions. It is well known that the *surface* dissymmetry in the earth's magnetic field is such that the line connecting the surface poles passes several hundred km to one side of the earth's center. The foregoing evidence that some such large dissymmetry extends thousands of miles above the surface is in strictness inconsistent with the idea of the existence of a "magnetic latitude" at all, since by definition this involves symmetry about a line passing through the earth's center. Even in the past there has been some uncertainty as to what position on the earth's surface should be taken as "the pole" from which to measure magnetic lattitude. The directly observed position of the north magnetic pole is at 70° N, 96° W, and the first term in the usual Fourier expansion, as made by Gauss, locates this virtual pole far away from the observed pole, namely, at 78° 30′ N, 69.08° W.

In view of this uncertainty, in our own work we tried to forget that we knew anything about the position of "a pole" and simply searched by the trial and error method for that point which when used as a pole would permit our readings, taken all around the globe, to remain everywhere as nearly as possible the same in the same latitude as measured from this point, the critical magnetic latitudes being between 25° and 40° where the sea level cosmic-ray intensity is varying most rapidly with northward or southward motion. We found that the largest degree of such consistency was obtained from our whole series of observations for a point very close to 78° N, 69° W and only a degree or two of departure from this point distinctly injured our consistency. So that the common practice of taking about this point from which to measure magnetic latitude is to a certain extent here experimentaily justified. The considerations here advanced, however, warn against expecting complete consistency in cosmic-ray readings along all so called magnetic latitude lines.

Synopsis

(1) The sea-level intensity of cosmic rays, obtained as a mean of observations lasting ten days in a given locality, is found to be 7 percent lower at the magnetic equator off Peru than in Los Angeles Harbor, and 8 percent lower than the mean value between Pasadena and Churchill, Manitoba, the beginning of the decline in intensity setting in sharply a few miles south of Pasadena in magnetic latitude 42. (2) Within the limits of observational uncertainty the change in sea-level intensity is symmetrical on both sides of the magnetic equator. (3) The corresponding decrease in sea-level intensity on the other side of the world, i.e., in going from magnetic latitude 42 to the magnetic equator in the neighborhood of Singapore, is 12 percent. (4) In going through the equatorial belt in an intermediate longitude as measured in voyages between Los Angeles and Sydney, Australia, the corresponding equatorial dip was found to have the intermediate value of 10 percent.

We desire to express our thanks to the Carnegie Corporation of New York and the Carnegie Institution of Washington, for providing the funds with the aid of which these researches have been carried out.

A Simplification of Prins' Formula for Diffraction of X-Rays by a Perfect Crystal

FRANKLIN MILLER, JR., *Ryerson Physical Laboratory, University of Chicago*

(Received December 18, 1934)

The intensity formula of Prins for diffraction of x-rays by a perfect crystal has been simplified so that $F(l)$ is a real, single-valued, algebraic function of l, the deviation of the glancing angle from the corrected Bragg angle. By neglecting absorption in the crystal, Darwin's formula is obtained in a new form. By differentiation the maximum ordinate of the diffraction pattern is obtained. To calculate percent reflection (i.e., maximum ordinate of the rocking curve of a double crystal spectrometer in the 1, −1 position) $\int_{-\infty}^{+\infty} F(l)dl$ and $\int_{-\infty}^{+\infty} F^2(l)dl$ are needed, and these integrals have been evaluated analytically for Darwin's case of no absorption, leading to a value of 4/5 for $P(0)$. To include absorption $F(l)$ has been expanded into a series in powers of B/D and an approximate formula obtained for $P(0)$ in terms of the constants of the crystal. This formula agrees with the graphically determined values of $P(0)$ to within a few percent.

INTRODUCTION

THE shape of the x-ray diffraction of a crystal is of some interest, since a knowledge of the variation of reflected intensity with glancing angle is an essential part of the theory of the x-ray spectrometer. Unfortunately, as shown by v. Laue,[1] the shape of the diffraction pattern cannot be observed directly with the double crystal spectrometer. The method of Smith[2] for calibrating a double-crystal spectrometer cannot be applied to calculation of the diffraction pattern, although it gives[3] the true shape of a spectrum line regardless of the diffraction pattern assumed. The method of checking any theoretical curve remains, therefore, to make observations upon related quantities such as half-width, percent reflection, etc., which can be calculated from the theory assumed, and hence obtain indirect evidence for or against the theory proposed.

In this manner Allison[4] and Parratt[5] have investigated the applicability of the Darwin-Ewald-Prins[6] theory of x-ray reflection from a perfect crystal and have observed specimens of calcite approaching "perfection" in the sense that the predictions of the theory are fulfilled over certain wavelength ranges.

In order to carry through the analysis for any crystal, a great deal of laborious calculation must be done and many graphical integrations performed. It is the purpose of this paper to give a simplification of the algebraic form of Prins' formula, so that the labor of computation is greatly reduced, and to apply approximate methods to some of the integrals involved in order to obtain an approximate formula for percent reflection in terms of the constants of the crystal.

SIMPLIFICATION OF PRINS' FORMULA

Using the notation of Parratt,[5] replacing his symbol A by the symbol D, we have for Prins' characteristic function

$$F(l)=I_l/I_0 = \left| \frac{(D+iB)/\delta}{l-i\beta/\delta \pm \{(l-i\beta/\delta)^2-[(D+iB)/\delta]^2\}^{\frac{1}{2}}} \right|^2, \quad (1)$$

where l is the only variable and is the deviation of the glancing angle from the corrected Bragg angle ($\theta=\theta_0+\delta \sec\theta_0 \csc\theta_0$) in units of $\delta \sec\theta_0 \csc\theta_0$. $F(l)$ is the ratio of intensity diffracted at an angular deviation l to the incident intensity. The constants of the crystal have been discussed in several places,[5, 7] and we will only note that B and β are related to μ_l so that for no absorption both are equal to zero. The constants may be calculated for any crystal; for λ2.299A on calcite in the first order $\beta/\delta=0.059$ and

[1] M. von Laue, Zeits. f. Physik **72**, 472 (1931).
[2] L. P. Smith, Phys. Rev. **46**, 343 (1934); L. P. Smith, paper at Pittsburgh meeting of the American Physical Society, 1934.
[3] L. G. Parratt, Phys. Rev. **46**, 749 (1934).
[4] S. K. Allison, Phys. Rev. **41**, 1 (1932).
[5] L. G. Parratt, Phys. Rev. **41**, 561 (1932).
[6] C. G. Darwin, Phil. Mag. **27**, 325 and 675 (1914); P. P. Ewald, Ann. d. Physik **54**, 519 (1917); P. P. Ewald, Phys. Zeits. **26**, 29 (1925); J. A. Prins, Zeits. f. Physik **63**, 477 (1930).
[7] A. H. Compton and S. K. Allison, *X-Rays in Theory and Experiment*, D. Van Nostrand and Co., 1935, page 375. ($F(l)$ is there given the notation $I'(l)$.)

$B/D=0.084$, and are less for shorter wavelengths.[8]

In Eq. (1) the square of the absolute value of the complex quantity must be formed, and the ambiguity of sign is to be resolved so that $F(l)\leq 1$. Upon multiplying the two values of $F(l)$ together, we see that

$$F_1(l)F_2(l)\equiv 1, \tag{2}$$

a result to be used later. We may write Eq. (1) as

$$F(l)=\left|\frac{l-i\beta/\delta\mp\{(l-i\beta/\delta)^2-[(D+iB)/\delta]^2\}^{\frac{1}{2}}}{(D+iB)/\delta}\right|^2, \tag{3}$$

and upon writing out the numerator and defining

$$\alpha^2=(D^2+\beta^2-B^2)/\delta^2 \tag{3a}$$

Eq. (3) becomes

$$F(l)=\delta^2(D^2+B^2)^{-1}|l-i\beta/\delta \mp\{(l^2-\alpha^2)-2i(\beta/\delta)(l+DB/\delta\beta)\}^{\frac{1}{2}}|^2. \tag{4}$$

We have

$$(A+iB)^{\frac{1}{2}}\equiv\pm[\pm\{\tfrac{1}{2}A+\tfrac{1}{2}(A^2+B^2)^{\frac{1}{2}}\}^{\frac{1}{2}} +i\{-\tfrac{1}{2}A+\tfrac{1}{2}(A^2+B^2)^{\frac{1}{2}}\}^{\frac{1}{2}}],$$

where the inner $\pm$ has the sign of B, so that we may write

$$F(l)=\delta^2(D^2+B^2)^{-1}|l-i\beta/\delta\pm\{\mp P^{\frac{1}{2}}+iQ^{\frac{1}{2}}\}|, \tag{5}$$

where P and Q are real functions of l and

$$P+Q=\{(l^2-\alpha^2)^2+4\beta^2(l+DB/\delta\beta)^2/\delta^2\}^{\frac{1}{2}}.$$

Thus, finally,

$$F(l)=\delta^2(D^2+B^2)^{-1}[l^2+\beta^2/\delta^2+P+Q \mp\{\pm 2lP^{\frac{1}{2}}-2\beta Q^{\frac{1}{2}}/\delta\}]. \tag{6}$$

Eq. (6) may be simplified considerably by defining

$$G(l)=\delta^2(D^2+B^2)^{-1}[l^2+\beta^2/\delta^2 +\{(l^2-\alpha^2)^2+4\beta^2(l+DB/\delta\beta)^2/\delta^2\}^{\frac{1}{2}}], \tag{7}$$

$$H(l)=\delta^2(D^2+B^2)^{-1}[\pm 2lP^{\frac{1}{2}}-2\beta Q^{\frac{1}{2}}/\delta], \tag{8}$$

so that making use of Eq. (2) we must have

$$[G(l)+H(l)][G(l)-H(l)]\equiv 1. \tag{9}$$

[8] In Parratt, Phys. Rev. **41**, 561 (1932), the fifth column in Table II on page 571 should be headed "B/δ" instead of "β/δ."

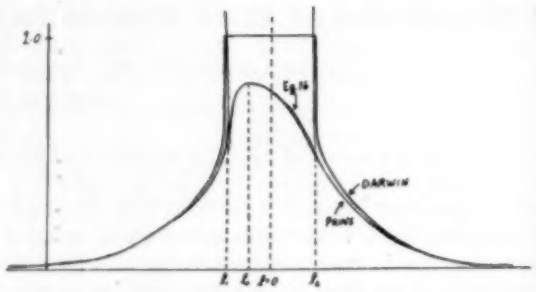

FIG. 1. Prins' function and Darwin's function (which neglects absorption) are plotted. Eq. (16) represents a series approximation to Prins' function which may be used between l_1 and l_2.

Hence $H(l)=\{G^2(l)-1\}^{\frac{1}{2}}$, and it may easily be shown that $G(l)\geq H(l)\geq 1$ for all values of l, so that for $F(l)$ we want $G(l)-H(l)$, or

$$F(l)=G(l)-[G^2(l)-1]^{\frac{1}{2}}. \tag{10}$$

$G(l)$, defined by Eqs. (7) and (3a), is real, positive, single-valued, ≥ 1 for all values of l, and involves only the square-root of a real, positive polynomial in l.

An alternative form of Eq. (10), adapted to rapid calculation, may be written as

$$F(l)=e^{-\psi}, \tag{11}$$

where

$$\cosh\psi=G(l). \tag{12}$$

Upon calculation of $G(l)$ for any angle, $F(l)$ may be found at once upon reference to ordinary tables of e^{-x} and $\cosh x$.

If $B=\beta=0$, we have Darwin's case of no absorption, and $\alpha^2=D^2/\delta^2$. For no absorption also $D/\delta=B/\beta=F/Z$, where F is the crystal structure factor and Z is the number of electrons per unit cell. Darwin's formula may therefore be written in the new form

$$F^D(l)=(F^2/Z^2)[l\mp\{l^2-F^2/Z^2\}^{\frac{1}{2}}]^2, \tag{13}$$

where the upper sign is for $l>F/Z$, the lower sign is for $l<-F/Z$, and for the region $-F/Z\leq l\leq +F/Z$ $F^D=1$ is to be used. $F(l)$ and $F^D(l)$ are plotted in Fig. 1, and it will be seen that the two differ markedly only in the region for which Darwin's theory predicts $F^D(l)=1$.

So far we have considered only σ-polarization of the incident beam, in which the electric vector is perpendicular to the plane of incidence. To obtain $F_\pi(l)$, D and B must be replaced by

$D\cos 2\theta_0$ and $B\cos 2\theta_0$, respectively, and for incident unpolarized radiation we will have $F(l)=\frac{1}{2}F_\sigma(l)+\frac{1}{2}F_\pi(l)$.

Calculation of Percent Reflection

Of the various theoretical predictions based upon the shape of $F(l)$, the percent reflection is perhaps the easiest to calculate and to measure. Defined as the ratio of the maximum intensity obtainable from the second crystal of a double crystal spectrometer in an $(n, -n)$ position to the maximum intensity upon that crystal, it is given[9] by

$$P(0)=\frac{\left(\int_{-\infty}^{+\infty}F_\sigma^2(l)dl+\int_{-\infty}^{+\infty}F_\pi^2(l)dl\right)}{\left(\int_{-\infty}^{+\infty}F_\sigma(l)dl+\int_{-\infty}^{+\infty}F_\pi(l)dl\right)}, \quad (14)$$

and for Darwin's case by

$$P(0)=\left(\int_{-\infty}^{+\infty}F_\sigma^2(l)dl\right)\Big/\left(\int_{-\infty}^{+\infty}F_\sigma(l)dl\right). \quad (15)$$

Using Eq. (13), it is a simple matter to evaluate the integrals for Darwin's case analytically, with the result that

$$\int_{-\infty}^{+\infty}F_\sigma^2(l)dl=32F/15Z;$$

the result

$$\int_{-\infty}^{+\infty}F_\sigma(l)dl=8F/3Z$$

had been obtained in 1914 by Darwin.[10] Dividing, we obtain $P(0)=4/5$, a result to be compared with the value 0.798 obtained by graphical integration of the numerator by Allison.[4]

For Prins' case, which includes absorption, a similar analytic expression could not be obtained, and if an accurate value of $P(0)$, half-width of the rocking curve, or coefficient of reflection R_c, is desired, graphical integration, made easier by the new form of $F(l)$, must be used. However, an approximate expression for the predicted value of $P(0)$ may be derived as follows:

[9] See reference 7, page 722, for a derivation of these expressions.

[10] C. G. Darwin, Phil. Mag. **27**, 675 (1914).

$F(l)$ is expanded into a power series in B/D, which vanishes with the absorption, using the binomial theorem and Eq. (10) or proceeding directly from Eqs. (11) and (12). The result is, for the region $-D/\delta<l<+D/\delta$, $(l^2<a^2)$,

$$F(l)=1-2d\frac{l+k}{(a^2-l^2)^{\frac{1}{2}}}+2d^2\frac{(l+k)^2}{a^2-l^2}+\cdots, \quad (16)$$

where for convenience we have written $d=B/D$, $a=D/\delta$, $k=\beta D/B\delta=a(\beta/B)>a$. Eq. (16) forms the first three terms of an exponential series, as might be expected from Eq. (12), and for Darwin's case $d=0$ and $k=1$, and $F(l)$ reduces to unity for this region, as it should.

For the outer regions, a similar series is obtained, lacking a term in d, accounting for the close agreement of Prins' function with Darwin's in these regions (see Fig. 1).

By differentiation of Eq. (16) is found that the series has minimum values equal to 0.5 for two values of l, $l_1=-a+2(k-a)^2d^2/a$ and $l_2=a-2(k+a)^2d^2/a$, and becomes infinite for $l=\pm a$. Thus the series may be used between these values of l, which are approximately at $\pm a$. Eq. (16) is plotted in Fig. 1.

To evaluate the integrals required in Eq. (14), series (16) is used between l_1 and l_2, and Darwin's formula (13) is used for the other regions. The areas neglected are small, depending upon d^2, and tend to compensate each other. In this manner the following expression is obtained:

$$P(0)=\frac{8N-2(1-6d^2)P+8QR-4S-11Q+U}{5(2+3d^2)N-P+2QR-S-4Q}, \quad (17)$$

where

$N=4a/15$,

$P=2kd[\sin^{-1}(l_2/a)+\sin^{-1}(-l_1/a)]$,

$Q=d^2(k^2+a^2)/a$,

$R=\tanh^{-1}(l_2/a)+\tanh^{-1}(-l_1/a)$,

$S=4kd^2\log_e[(k+a)/(k-a)]$,

$U=16k^2d^4\{3+(k^2/a^2)\}/a$;

$-l_1/a=1-2d^2(k-a)^2/a^2$,

$l_2/a=1-2d^2(k+a)^2/a^2$;

and

$a_\sigma=D/\delta$; $a_\pi=(D/\delta)\cos 2\theta_0$,

$d_\sigma=d_\pi=B/D$; $k_\sigma=k_\pi=(\beta/B)a=\beta D/B\delta$.

As given in Eq. (17) σ-polarization only is considered. To correct for this the numerator and denominator must be written as sums of two terms, one using a_σ, d, and k throughout, and the other using a_π, d, and k. However it probably is not worth the trouble, as Eq. (17) gives results to about 5 percent without making the correction.

For $\lambda 2.299$ on calcite, Parratt[5] obtains for the calculated percent reflection $P(0)=57.8$ percent, using graphical integration. Eq. (17) gives as an approximation to this calculated value $P(0)=60.8$ percent without making the correction, and $P(0)=60.5$ percent when polarization is considered. Series (16) represents Prins' function best for fairly soft x-rays, when $F(\pm a)$ is close to 0.5, and this is exactly the region where agreement of *experiments* with Prins' function seems best.[6] Eq. (17) is therefore useful for checking rapidly the percent reflection according to Prins' theory, and as a test of the perfection of a particular crystal specimen referred to Prins' theory a fairly long wavelength should be used, not too close to a critical absorption limit of the crystal.

The experimental results of Parratt[5] tend to show that the percent reflection is much more sensitive to slight imperfections of the crystal than is the half-width of the rocking curve, so that the means of estimating the calculated percent reflection outlined above should be useful in judging the degree of perfection of a crystal specimen.

The method of computation given in Eqs. (10) to (12) is exact, and makes it very much easier to compute the curves, should graphical integrations be deemed necessary.

It is interesting to note that since $F(l)$ in the exact (Prins) form has been reduced to an ordinary real algebraic function of l, its derivative may be set equal to zero and the maximum ordinate calculated. It is readily found from Eq. (10) that the maximum ordinate of the diffraction pattern occurs for $l_0=-BD/\beta\delta$ for σ-polarization and for $l_0=-(BD/\beta\delta)\cos^2 2\theta_0$ for π-polarization. The maximum ordinate is $F_\sigma(l_0)=[(\beta^2+D^2)^{\frac{1}{2}}-(\beta^2-B^2)^{\frac{1}{2}}]^2/(D^2+B^2)$, with a corresponding expression for $F_\pi(l_0)$. These reduce to unity for no absorption, as they should, and serve to give a rapid estimate of the extent of deviation of Prins' function from Darwin's ideal case.

The author wishes to express his appreciation of stimulating and helpful discussions with Professor S. K. Allison concerning many of the concepts involved in this paper.

Band Spectrum of Barium Hydride at 10,000A

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A BaH band with principal head at 10,052A degraded to the red is $(0,0)\,^2\Pi_{1\frac{1}{2}}\rightarrow{}^2\Sigma$, the lower state being the same as for the other BaH systems. $B_0''=3.280$, $D_0=-1.3\times10^{-4}$ and the Λ-doubling is large and negative. This $^2\Pi$ state as well as the upper $^2\Sigma$ state for the 8924A band must be derived from Ba $^2P+\mathrm{H}\,^2S$. The origin of a perturbation in the $^2\Pi_{1\frac{1}{2}e}$ levels at $J=20\frac{1}{2}$ is discussed.

IN a recent investigation[1] the existence of a BaH band with principal head at 10,052A degraded to the red was noted. The sign and magnitude of the spin doubling of the upper $^2\Sigma$ state of the $^2\Sigma\rightarrow{}^2\Sigma$ bands at 8924A indicated strong interaction with a near-lying lower $^2\Pi$ state which might be involved in the bands on the long wavelength side of 10,000A. Using an Eastman 144-Q plate, a spectrogram with BaH lines out to 10,250A has now been obtained. Analysis shows these to belong to the $^2\Pi_{1\frac{1}{2}}$ portion of a $^2\Pi\rightarrow{}^2\Sigma$ band, having the same lower state as the other BaH band systems[1-3] and with an upper state which displays through its large Λ-doubling the suspected interaction with the neighboring $^2\Sigma$ state. Though incomplete because of the limitations on the photography of spectral lines of low intensity in this infrared region, these measurements yield sufficient information as to the character and position of this new BaH state. The light source was a 220-volt d.c. arc carrying 2 amperes between a water-cooled copper anode and a hollow copper cathode filled with metallic barium in an atmosphere of hydrogen at about 5 cm pressure. The exposure time was six hours, using the first order of the 21-foot concave grating in a stigmatic mounting which gives a dispersion of 4.7A/mm.

Table I contains the quantum assignments of the frequencies in this band. J'' values were first assigned to the lines of the prominent ${}^sR_{21}$ and Q_2 branches by means of the combination differences ${}^sR_{21}(J)-Q_2(J+1)=T_2''(J+1)-T_1''(J)$ obtained from the $^2\Pi\rightarrow{}^2\Sigma$ band in the visible red region. The identity of these differences in the two bands as given in Table II shows this to be a $^2\Pi_{1\frac{1}{2}}\rightarrow{}^2\Sigma$ (0,0) band with the same lower state for both bands. R_2- and ${}^RQ_{21}$-branch assignments were then made principally with the aid of the known lower-state spin doubling values. A few P_2- and ${}^QP_{21}$-branch lines of low intensity for small J values are observed, but since they fall in the region which contains many lines of the R_2 and ${}^RQ_{21}$-branches of the (1,1) band, we do not consider their assignment definite enough to justify inclusion in Table I.

TABLE I. *Assignment of frequencies for the 10,052A (R_2 head) $^2\Pi\rightarrow{}^2\Sigma$ (0,0) BaH band. cm^{-1} units.*

$J''+\frac{1}{2}$	${}^sR_{21}$	Q_2	${}^RQ_{21}$	R_2
4	9951.24	9895.49		9924.89
5	60.30	91.76	9924.50	27.89
6	69.26	87.93	26.81	30.29
7	78.16	83.79	28.91	32.50
8	86.74	79.43	31.09	34.74
9	95.18	75.02	33.02	36.50
10	10003.49	70.53	34.74	38.39
11	11.57	65.81	36.33	39.88
12	19.45	60.92	37.71	41.26
13	27.06	56.14	38.90	42.42
14	34.47	50.97	39.88	43.35
15	41.61	45.64	40.49	44.08
16	48.48	40.20	41.17	44.61
17	55.06	34.60	41.35	44.70
18	61.36	28.75	41.35	44.61
19	67.19	22.57	41.17	44.08
20	72.15	16.14	40.49	43.53
21	83.31	08.86	39.88	42.82
22	86.79	07.91	38.90	41.98
23	91.18	799.60	37.71	
24	95.58	92.19		
25	99.88	84.87		
26	103.89	77.47		
27	07.49	70.16		
28	10.78			
29	13.91			
30	16.50			
31	18.68			
32	20.59			
33	22.24			
34	23.37			

The rotational energy term constants for this

[1] W. W. Watson, Phys. Rev. **43**, 9 (1933).
[2] W. R. Fredrickson and W. W. Watson, Phys. Rev. **39**, 753 (1932).
[3] A. Schaafsma, Zeits. f. Physik **74**, 254 (1932); G. Funke, Zeits. f. Physik **84**, 610 (1933).

TABLE II. *Combination differences in the 10,052A $^2\Pi_{1\frac{1}{2}} \rightarrow {}^2\Sigma$ BaH band.*

$J''+\frac{1}{2}$	$^SR_{21}(J)-Q_2(J+1)$ 10,000A	6730A	$\Delta_2T_{2c}'(J)$	$\Delta_2T_{2d}'(J)$	$\Delta\nu_{dc}$
4	59.48	59.48			
5	72.37	72.49			−0.07
6	85.47	85.29	78.52	78.25	+0.14
7	98.73	98.59	91.44	91.33	−0.14
8	111.72	111.70	104.35	104.71	−0.27
9	124.65	124.64	117.33	117.07	−0.13
10	137.68	137.66	130.24	129.98	−0.39
11	150.65	150.51	142.99	142.58	−0.42
12	163.31	163.26	155.78	155.55	−0.58
13	176.09	175.95	168.47	168.35	−0.64
14	188.83	188.70	180.84	180.65	−1.00
15	201.41	201.36	193.34	191.95	−1.15
16	213.88	213.86	205.72	205.56	−1.30
17	226.31	226.33	217.93		−1.49
18	238.79	238.70	230.02		−1.91
19	251.05	251.00	241.88		−2.21
20	263.29	263.23	253.21		−2.55
21	275.40	275.30	270.98		
22	287.19	287.35	281.93		
23	298.90	299.03	287.46		
24	310.71	310.51	300.35		
25	322.41	322.62	312.25		
26	333.73	334.00	323.76		
27			334.95		
28			345.74		

$^2\Pi_{1\frac{1}{2}}$ state may be determined, however, from the frequencies given in Table I together with lower-state differences obtained from the data for the red BaH bands. For $\Delta_2T_{2c}'(J)=\,^SR_{21}(J)-Q_2(J-1)-T_2''(J-1)+T_1''(J)$ and $\Delta_2T_{2d}'(J)=R_2(J)-\,^RQ_{21}(J-1)+T_1''(J-1)-T_2''(J)$. The values of these term differences are given in Table II. Using the mean values of these two sets of differences, we compute in the usual way that $B_0^*=3.280$ and $D_0=-1.3\times10^{-4}$. In order to determine the magnitude of the Λ-doubling, the values of $\Delta_1T_{2c}'(J+\frac{1}{2})$ are first calculated with the B and D constants given by the $\Delta_2T_{2c}'(J)$ differences. Then the Λ-doublet width $\Delta\nu_{dc}(J+1)$ is $R_2(J)-Q_2(J)-\Delta_1T_{2c}'(J+\frac{1}{2})$. The values of $\Delta\nu_{dc}$ so calculated are given in the last column of Table II.

In Fig. 1 the variation of these Λ-doublet widths with J is given by the solid curved line. Whereas for the red $^2\Pi\rightarrow{}^2\Sigma$ band this doubling in the $^2\Pi_{1\frac{1}{2}}$ levels is small and positive,[4] the Λ-doubling here is several times larger and negative. Assuming that a relation of "pure precession"[5] with $l=1$ holds between this $^2\Pi$ state and the upper $^2\Sigma$ state of the 8924A band, one may compute the value of this Λ-doubling as a function of J if the coupling constant A of the $^2\Pi$ state is known.[2] Taking[1] $A=640$, $p=-4.84$ ($=\gamma_0$ of the $^2\Sigma$ state) and $\nu(\Pi,\Sigma)=-1500$ cm^{-1} ($q=-43/1500$), the Λ-doublet widths represented by the dashed curve in Fig. 1 have been calculated. The trend in the two curves is the same, and quite possible variations from the values of the constants assumed in this calculation would make the difference between the curves negligible. It is to be concluded, then, that these two BaH states are the two which are derived from Ba ^3P+H ^2S.

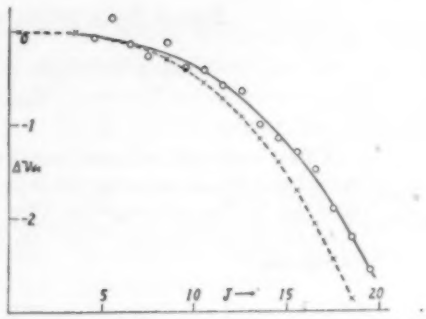

FIG. 1. Λ-doublet widths in the $^2\Pi_{1\frac{1}{2}}$ levels of the 10,052A BaH band. Solid line represents observed values, broken line those computed assuming pure precession relation with $l=1$ to hold between this state and the upper $^2\Sigma$ state of the 8924A band.

A rather large perturbation, observable in the $^SR_{21}$ and Q_2 branches, occurs in the $^2\Pi_{1\frac{1}{2}c}$ levels at $J=20\frac{1}{2}$. Since the dissociation energy of the ground $^2\Sigma$ state may be as large as 1.4 volts, the perturbing levels may be in one of its higher vibrational states. The only other possibility for levels at this energy above the minimum of the ground state is that they occur in a . . . $5d\delta\,{}^2\Delta$ state lying below this . . . $6p\pi\,{}^2\Pi$. This $^2\Delta$ state may well lie below the . . . $6p\pi\,{}^2\Pi$, for the $5d\,{}^3D$ level is lower than the $6p\,{}^3P$ level in the Ba atom. The fact that a perturbation apparently does not occur in the $^2\Pi_{1\frac{1}{2}d}$ levels at or near this same J value does not favor either one or the other of these two possibilities.

[4] Reference 2, Fig. 2.

[5] R. S. Mulliken and A. Christy, Phys. Rev. **38**, 87 (1931).

The Ultraviolet Absorption Band of Li_2

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Ultraviolet band systems of lithium have been observed and a vibrational analysis suggested which involves four upper states.

Assuming that these upper states have the same dissociation limit, values of D' have been calculated and compared with corresponding values of D' for the upper states of sodium.

BAND systems due to the lithium molecule in the blue-green and the red portions of the spectrum have been observed and analyzed by several investigators,[1] and some indication of the existence of ultraviolet bands has been noted.[2] Since such bands of lithium might be expected in view of the known ultraviolet band systems of sodium[2, 3] it seemed of interest to make an attempt to measure and analyze them.

EXPERIMENTAL

The absorption tube was of steel, 110 cm in length with a diameter of 2.5 cm. Quartz windows were waxed on the ends, and the ends were water-cooled. The steel tube was insulated with alundum cement and nichrome ribbon wound on this. A side tube allowed the system to be evacuated. After the lithium had been placed in the furnace and thoroughly evacuated, heating was begun, and about 20 mm pressure of helium added to retard diffusion of the lithium to the cold ends. To obtain a suitable pressure of lithium in the tube the temperature was raised to 800–950°C. The light source above 3100A was a tungsten lamp, and below 3100A a hydrogen discharge was used.

Observations were made on a Schmidt and Haensch Universal Spectrograph with two quartz prisms and a telenegative lens. In the region where bands were found the dispersion was about 3.3A per mm.

The bands were measured on several plates by means of a Leiss comparator, which had an accuracy of about ±0.01 mm and also on a comparator belonging to the Physics Department, which could be read to ±0.001 mm. The bands were, of course, not sufficiently sharp to warrant the use of the more accurate instrument, but a comparison of the observed frequencies thus measured, allow us to estimate the accuracy of the frequencies as being ±2 cm^{-1} on the whole.

RESULTS

Some sixty band heads were measured in all. These bands degrade to the red, as do the other lithium bands, and arise from the same ground state, $^1\Sigma_g^+$. In order to account for the large number of band heads it has been assumed that there are four upper states which give rise to these bands. In the corresponding case of sodium five upper states were assumed,[3] to account for the measured heads.

The proposed assignments are listed in Tables I, II, III, IV. Equations can be found to reproduce the values shown in both Table I and II of the form

$$\nu_{\text{head}} = \overset{0,\ 0}{\nu_{\text{head}}} + [a_h' v' - b_h' v'^2] - [a_h'' v'' - b_h'' v''^2] + \theta v' v''.^4 \quad (1)$$

For Table I, the equation is:

$$\nu_{\text{head}} = 30501.2 + [231.2v' - 2.1v'^2] - [351.3v'' - 3.0v''^2] \quad (2)$$

and for Table II,

$$\nu_{\text{head}} = 30886.2 + [210.2v'] - [349.2v'' - 2.9v''^2]. \quad (3)$$

The wave numbers in Tables I and II have

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[1] See, for example Jevons *Report on Band Spectra of Diatomic Molecules*, p. 282.

[2] Walter and Barratt, Proc. Roy. Soc. (London), **A119**, 257 (1928).

[3] Weizel and Kulp, Ann. de Physik (5), **4**, 971 (1930).

[4] Jevons, *Report on Band Spectra of Diatomic Molecules*, p. 57.

Proposed assignment of lines in the spectrum of Li_2.

TABLE I. $\nu_{head} = 30501.2 + (331.2v' - 2.1v'^2) - (351.3v'' - 3.0v''^2)$.

v' \ v''	0	1	2	3	4	5
0	30501.1	30150.9	29810.7	29474.9	29136.2	
1	30729.3	30386.5		29700.4	29364.5	29038.0
2	30954.3	30607.1		29921.1		
3	31173.3		30492.8			
4	31396.4	31047.7				
5		31274.2				

TABLE II. $\nu_{head} = 30886.2 + 210.2v' - (349.2v'' - 2.5v''^2)$.

v' \ v''	0	1	2	3	4
0	30886.2	30538.8		29866.9	
1		30750.3	30408.2	30082.5	29746.5
2			30618.8		29959.2
3		31170.3		30492.2	
4	31722.8	31380.7			

TABLE III.

v' \ v''	0	1	2	3	4	5	6	7	8
0			30687.2		30020.7	29695.2	29377.1	29066.0	28758.1
1		31286.2		30604.2	30275.0	29954.4			
2	31898.7	31547.9				30209.6	29884.3		

TABLE IV.

v' \ v''	0	1	2	3
0	31898.7	31547.9		
1		31773.3	31431.4	
2		32003.0	31652.3	31316.3
3				31541.3

already been corrected by the value of $\theta v'v''$. System I, $\theta = 0.2$ cm^{-1}, System II, $\theta = 1.0$ cm^{-1}.

Eqs. (2) and (3) indicate values for the upper state entirely comparable with those of previous workers. McKellar[5] gives the value $\Delta G_v'' = 351.374 - 5.181(v'' + \frac{1}{2})$. The agreement tends to verify the assignments as made.

[5] McKellar, Phys. Rev. **44**, 155 (1933).

These bands are grouped around the second member of the principal series of the lithium atomic lines, at 30925.9 cm^{-1} which corresponds to an excitation of the atom from the $2\,^2S$ ground state to the $3\,^2P^0$ state. Assuming that all of the upper states involved in the ultraviolet band systems of the molecule have the same dissociation products, that is, one $2\,^2S$ atom and one $3\,^2P^0$ atom, it is possible to calculate D', the energy of dissociation of the molecule in each of these four upper states. The energy of dissociation, D'', of the molecule in the ground state has been calculated to be 1.14 v[6] and the energy of excitation of one atom from a $2\,^2S$ to $3\,^2P$ state is 30,925.9 cm^{-1} or 3.82 v.[7] The four values of D' are then found to be 1.19 v, 1.14 v, 1.08 v and 1.02 v corresponding to the systems represented in Tables I, II, III and IV, respectively. Comparable values of D' for the five upper states of the ultraviolet sodium band systems[3] can be calculated. They are as follows for the system indicated in the reference, $A \rightarrow B'$, 0.84 v; $A \rightarrow C'$, 0.73 v; $A \rightarrow D$, 0.63 v; $A \rightarrow B''$, 0.37 v; $A \rightarrow C''$, 0.31 v. The ratio of the values of D' for comparable systems of sodium and lithium is closely the same here as in the red and blue-green systems of the two elements.

The lithium atom has, as well, a $3\,^2D$ state with nearly the same energy as the $3\,^2P$ state. The atomic line corresponding to an excitation from the ground state to the $3\,^2D$ state was not observed, but if this state is involved in the production of any of the band systems, the energy of dissociation as calculated will be too low by 0.04 v.

The observed bands fall in the range λ3100 to λ3500. The region below λ3100 was investigated down to the series limit of the atomic spectrum, but no further band systems were observed.

It is a pleasure to thank Professor W. W. Watson of the Sloane Physics Laboratory for his very helpful interest and advice.

[6] Loomis and Nusbaum, Phys. Rev. **38**, 1447 (1931).
[7] Bacher and Goudsmit, *Atomic Energy States*, p. 264.

On the Redward Shift of Spectral Lines of Nebulae*

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The characteristics of a wave traveling in a medium in which the velocity of light is a function of time is considered and it is shown that one is able to account for the redward shift of spectral lines from distant nebulae on this basis. For simplicity, the function $c_1=c(1-\alpha t)$ is assumed and numerical calculations are made yielding a value of $\alpha=1.81\times10^{-17}$ cm per sec. as being necessary to account for observed redward shift.

THE redward shift of spectral lines of nebulae has been the basis of much speculation in recent years. Next in importance to the experimental fact of the shift itself is the shift-distance relationship announced by Hubble and Humason,[1] according to which the redward shift is proportional to the distance to the nebula.

The theory most commonly heard for explaining these observations is that in which the shift is interpreted in terms of the Doppler effect, implying a recession of the nebulae with velocities proportional to their distances. Other attempts have been made to account for the phenomenon. For example, Zwicky[2] suggests that there may be a "gravitational drag" on light; Milne[3] proposes a certain kinematical model and MacMillan suggests that there may be, in some unaccounted manner, a loss of energy by the photon in its long journey through space. Another explanation is offered herewith as one which has the advantage of considerable simplicity and avoids the necessity of an "expanding universe." It is based on the assumption that the velocity of light throughout space changes slowly as a function of time.[4]

At least in the special relativity, the velocity of light has been considered as a fixed and constant property of space, but this is itself an assumption and we have not had nearly sufficient time over which to take observations to either prove or disprove such an assumption. In the general relativity theory, there is less ground for assuming the constancy of the velocity of light with time, as pointed out by Vrkljan.[5] And, finally, in developing the theory below, it is not necessary to consider that the velocity of light in a matter free, field free space is changing, for it will be sufficient if we can think of the matter content or the field content as changing and so producing, in some manner, a change in velocity. With this preliminary statement the line of reasoning would run along as follows:

Let us consider the case of a source of light and an observer, separated by a distance D.

$$S \qquad D \qquad O$$

We will allow light to pass from S to O with constant velocity establishing a train of waves, the number of these waves being given by $N=D/\lambda=\nu t$, where ν is the frequency at the source and t is the time for light to travel the distance D. Let us assume that in some way the velocity of light suddenly changes from c to c_1, where for definiteness c_1 is less than c. In this process the length of the waves between S and O is not changed for the velocity of each element of the wave changes at the same time by the same amount. The rate, however, at which they thereafter proceed towards the observer, is reduced and the number of waves which will reach the observer per unit of time is reduced. The time required for the N waves to sweep through to the observer will be increased to t_1 where $t_1=D/c_1$ and the rate of arrival of waves will be $N/t_1=\nu t/t_1=\nu c_1/c$. This new rate of arrival of waves will persist until the train of waves standing in the space at the moment of change of velocity has swept out, and there would be a redward shift of spectral lines. After

* The contents of this paper were presented at a meeting of the American Physical Society in New York City, Feb. 23, 1934.

[1] Hubble and Humason, Astrophys. J. **74**, 43 (1931).

[2] F. Zwicky, Proc. Nat. Acad. Sci. **15**, 773 (1929).

[3] Milne, Nature **130**, 9 (1932).

[4] The change of velocity of light here contemplated is not related to the alleged changes discussed by de Bray in Nature **127**, 522, 739, 892 (1931) and elsewhere, but is of an entirely different order of magnitude, being very much smaller.

[5] Vrkljan, Zeits. f. Physik **63**, 688 (1930).

this interval, however, the rate of arrival will be restored to the original rate, although the wavelength will be shorter.

A more important case is that in which the velocity changes continuously rather than suddenly and for this discussion the more interesting as well as the simplest case is that in which the velocity changes linearly with respect to time. For simplicity let us consider that this change is a decrease so that the velocity of light at any time is given by $c_1=c(1-\alpha t)$ where c is the velocity of light throughout space when $t=0$. Let frequency of the source $=\nu$. Then the number of waves, at $t=0$, in 1 cm at source is $n=1/\lambda=\nu/c$.

Let $t_1=$time to travel distance D to observer O with the changing velocity. At that time, then, the velocity is $c_1=c(1-\alpha t_1)$. The length of any particular wave, having once started, is not changed and the waves in the original 1 cm train $=n=\nu/c$. The time for this group to pass the observer is $1/c_1$. $\therefore$ the new rate of arrival is $\nu_1=n/(1/c_1)=nc(1-\alpha t_1)=\nu(1-\alpha t_1)$ or $(\nu-\nu_1)/\nu=\alpha t$ and thus there is a redward shift which is proportional to the time since the wave left its origin. If α is small $t_1=D/C$ approximately and $(\nu-\nu_1)/\nu=\alpha D/c$. Thus it is seen that the original simple assumption leads one definitely to a redward shift which is proportional to the distance to the source and this is in agreement with the Hubble Humason observations.

The shift has been considered above in terms of change in frequency of the arriving wave. It may be argued that in our optical work, as with gratings, we measure wavelength and not frequency. Consideration from this point of view leads to the same redward shift. Thus the sodium line emitted by a source in our laboratory has a certain wavelength λ'. Sodium light from a star a million years away was emitted at a time when the velocity of light was greater by the factor $(1+\alpha t)$ and the wavelength λ'' was therefore longer, given by $\lambda''=\lambda'(1+\alpha t)$. Since this wave, having once been started on its journey, remains constant in length, it arrives at the grating longer than the locally produced wave by the factor $(1+\alpha t)$. Thus $(\lambda''-\lambda')/\lambda'=\alpha t=\alpha D/c$ as before.

Let us now estimate the value of α for light from the nebulae. Hubble and Humason conclude from their Mt. Wilson observations that there is an apparent velocity of recession of 558 km/sec. for a nebula 1 million parsecs. (3,259,000 light years) away. This is calculated from what amounts to a redward shift of 12.2A for the $H\alpha$ line of 6562.8A. But $(\nu-\nu_1)/\nu=(\lambda_1-\lambda)/\lambda_1=\alpha t$, $\therefore$ $\alpha t=12.2/6575=1.87\times10^{-3}$ so that $\alpha=1.87\times10^{-3}$ for a unit of time corresponding to 10^6 parsec.

For other units of time α is given as follows:

Unit of time	α
3.259 years	1.87×10^{-9}
1 year	5.72×10^{-10}
1 sec.	1.81×10^{-17}

If we accept the work of Hubble and Humason as showing that the redward shift is proportional to the distance, then, on the basis of the present theory, we must conclude that the uniform decrease in velocity has been going on at least as recently as the time to the nearest star or nebula for which redward shift has been determined and for as long a time as that to the most remote nebula for which the redward shift has been observed, i.e., for some 150 million years.

It will be noted that if this rate of decrease continues, the velocity of light will be zero after about 1.7×10^9 years. The difficulty is reduced if we assume that the velocity of light is a periodic function of time and that for a long period we have been on a nearly linear portion of the velocity-time curve. While it does not appear now it may develop, on more complete measurements, that the redward shift is not strictly proportional to the distance and in that event it would not be necessary to assume that the velocity has been changing at a constant rate over the past 150 million years.

It has been suggested that it would be helpful in accounting for the redward shift if we could find a "photon leak." There has, however, been no satisfactory proposal as to how this leak might occur. The theory above seems to offer a simple explanation of how a photon may lose energy. For if the frequency of emission is ν then the photon energy is $h\nu$. As a result of the decrease of velocity during transit the rate of receipt of waves becomes ν_1. The wavelength for that train remains constant and the apparent photon energy is $h\nu_1$. The corresponding loss in photon energy is associated with the loss of

velocity, for $h\nu = hc/\lambda$ and $h\nu_1 = hc_1/\lambda$ and thus a decrease in velocity appears to carry with it a "photon leak."

It may be argued that if one desires some other explanation than the Doppler principle for the redward shift there is no reason for selecting the velocity of light as the "victim" but that one might equally well assume that our units of length or our units of time are changing. So far as the unit of length is concerned it should be noted that it is not a case where we measure the wavelength of nebular light at the time of its emission, say 10^8 years ago, and compare it with the wavelength of light emitted now during which 10^8 years our meter stick may have changed but that we are comparing two wavelengths, one an "old" one and the other a "young" one and are doing this today with the same meter stick and the outstanding experimental fact is that the wavelengths are different.

The same argument applies to a possible change in time units. We are comparing the frequency or the time of vibration *today* of two waves, one of ancient origin and one of recent origin and we are determining these with the same time unit. Again the outstanding observational fact is that the frequencies, as measured today against any unit of time, are different. One may, of course, contemplate some more subtle change in unit of time than that above but this could lead only to the conclusion that the frequency of oscillation, corresponding, say, to a Na atom, has changed in the meantime; but to abandon the idea of the constancy of frequency as a characteristic of an atom and as a reliable unit of time is a very difficult thing indeed.

It must be admitted that the theory given above as an explanation of redward shift is subject to criticism because of its high degree of ad-hocness and can be justified only if it finally connects up with other phenomena or suggests useful experiments. As a step in this direction it may be pointed out that a change in velocity of light in space as a function of time does not necessarily carry with it the idea that the velocity in matter free, field free space is variable.[6] It occurs to one, for example, that the permeability and the dielectric constant, and therefore the velocity, may be dependent slightly on radiation density. No suggestion of such dependence is indicated by Maxwell's equations but this, of course, is because no physical concept corresponding to this was included in the original framework of his problem and therefore cannot be present in the final result. We have become quite accustomed to the idea of matter turning into radiation and in recent years we are becoming familiar with the thought of radiation going into matter. If these processes are going on it is not at all probable that they are proceeding at the same rate and thus we conclude that radiation density throughout space is, on the whole, increasing or decreasing. If, then, it should develop that the velocity is a function of radiation density we would have a satisfactory basis for the explanation of the redward shift of nebular lines. It is not, of course, to be assumed that such changes would be exactly the same in all parts of the universe; but any departure from uniformity would imply a departure from the Hubble Humason law. Present uncertainties, however, as to the distances to nebulae do not permit an answer on this point.*

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[6] The suggestion has been made that such changes in velocity as indicated above might be due to thinly dispersed matter. This view is not tenable for it would mean that the amount of such matter has been increasing for the past 10^8 years or more. During that time the "index of refraction" of space on this theory has changed by the amount $5.72\times10^{-10}\times10^8 = 5.72\times10^{-2}$. This is about 200 times as great as the change in index due to a normal atmosphere of air.

* Since preparing this article my attention has been called to an article by Gramatzki, Zeits. f. Astrophys., Apr. 1, 1934, in which he endeavors to derive the equation of a wave in such a medium as is here considered. Unfortunately the equation he obtains seems to be incorrect. This will be taken up in an article to appear soon.

A Temperature Variation Method to Assist in Vibrational Analyses of Complex Molecular Spectra

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A temperature variation method of determining the initial (lower) vibrational levels of the absorption bands of an electronic band system of a polyatomic molecule is presented. The determination is made from photometric measurements of the absorption at two temperatures not widely separated. Such absorption tube lengths are used that the absorption is everywhere much less than 100 percent in the bands to be studied. That variations in total absorption for a band may be measurable, the method is restricted to spectra in which the rotation lines are fairly broad compared with the intervals between them or else are very closely spaced. In such cases the rotational structure is blotted out on the photographic plate by the lack of resolution of the spectrograph and the exponential absorption law may be assumed in comparing absorption intensities at the two temperatures. A criterion is laid down for the applicability of the method in any instance. An equation is developed to give the heights (in cm^{-1}) of the excited vibrational levels of the normal electronic state involved in the various transitions, above that of some arbitrarily selected band of a group, as follows:

$$\log_{10}\rho_b/\rho_a = -0.623\left(\frac{1}{T_2}-\frac{1}{T_1}\right)(G_b-G_a)''.$$

The determination of the heights $(G_b-G_a)''$ in cm^{-1} comes from the two absolute temperatures and the ratio ρ_b/ρ_a of the heights of the absorption peaks on the two microphotometer traces.

INTRODUCTION

IN the literature casual mention of the use of temperature variation to assist in the analysis of complex molecular absorption spectra is often found. The information that certain bands are associated with transitions from the normal state, while others occur from excited states whose heights above the normal state may be more or less closely estimated, may well bring order into an otherwise hopeless maze of frequencies. This information can be obtained from a systematic comparison of the relative changes in intensities of absorption of the different bands with temperature. A simple procedure applicable to a vibrational analysis in the photographic range will be presented here. The method is designed for use with closely spaced rotational structures appearing as unresolved band envelopes on the spectrum photograph. Its application could be extended to include molecules whose rotational structure can be blotted out by pressure.

The procedure is to seal off an appropriate mass of gas in an absorption tube and take plates of the absorption at two temperatures not widely separated. An extension is readily made to the investigation of a gas that dissociates under the energy of the continuous light source and must be flowed through the absorption chamber. To keep the same number of molecules in the light path under the two temperatures requires in this case an adjustment of pressure in conformity with the gas laws. The gas can be heated before admission to the tube and the pressure can be regulated by the valves controlling its rate of admission and exhaustion.

CRITERION OF APPLICABILITY OF THE METHOD

With N absorbing molecules in the light path, we have for gas absorption the exponential law

$$I = I_0 e^{-\mu(\nu)N},$$

where $\mu(\nu)$ is the absorption coefficient of the material per molecule for frequency ν; I is the intensity of light of frequency ν transmitted by the gas and I_0 that incident on the gas chamber. This is the law for the ideal case of a single frequency under perfect resolution. But the absorption intensity of a line M is defined as $\alpha_M = \int_M \mu(\nu)d\nu$, and moreover plates of polyatomic vibration-rotation bands usually consist of partially resolved rotation lines. Under relatively high dispersion the rotational structure may be partially distinguishable while with low dispersion instruments only an envelope of unresolved structure is observed. In either event, since the absorption coefficient of the gas varies greatly in a very small frequency range among the band lines, the limits of usefulness of the exponential law must be examined.

In the spectrum of HCL, for example, in which the band lines are narrow compared with the intervals between them, this law cannot be expected to hold in gross. In infrared work Bourgin[1] showed that it is inapplicable to a single band line directly under ordinary working conditions. The apparent failure of the law was accounted for on the basis that the resolving power of the spectrometer with the slit widths used was not sufficient to give the true shapes of the absorption curves. In the type of spectrum for which the present method is proposed, namely, for closely spaced rotational lines, the slit width is large enough to include a number of lines. Thus much overlapping occurs on the spectrum photograph and the shapes of the individual absorption lines are completely blotted out. If the overlapping is sufficient the exponential law may now hold in gross, at least the gross effects may be comparable at two temperatures relatively close together.

If the rotation lines are broad compared with the distances between them, a small change of temperature will produce a measurable change in the intensity of absorption of the apparent band envelopes. Further, under such temperature variation the shapes of the rotation lines, hence of the envelope resulting from the overlapping, should not be sensibly altered provided the slit width remains the same. If the exponential absorption law is to be applicable, it is clear that the absorptions at all positions of maximum absorption coefficient, that is at the centers of the band lines, must be kept small compared with 100 percent (Dennison[2]). The validity of its application is subject to experimental check in any given case. Keeping the temperature constant, the absorption tube may be filled with the gas at two pressures such that the amounts of absorption are about the same as in the two spectrum photographs in which the temperature is varied. The criterion of applicability of the method is then that the heights of all peaks on the two microphotometer traces corresponding to the two pressures shall be proportional to these pressures.

When this criterion is obeyed, the necessity of using the technique employed by Bartholomé[3] (namely, broadening the band lines under pressure until little trace of the original structure remains) is avoided. It seems then that if the band lines either are naturally broad and diffuse or if they are so closely packed that the intervals between them are small the required conditions are fulfilled. This situation has apparently been encountered in the spectrum of sulphur dioxide (see paper following). It is to be expected that this will also be the case for a number of polyatomic molecules, while with other molecules the application of moderate pressure to the gas may make the absorption amenable to the criterion for the validity of the exponential absorption law.

The Photographic Plate and the Microphotometer

The theory of the method, involving the use of the microphotometer, will now be developed. The photographic plate, which is the basic element in the process, is discussed in a number of places.[4] "Density" may be represented on the straight line portion of a characteristic curve for a plate by

$$D = \gamma(\log_{10} E - \log_{10} i),$$

where γ is the "contrast factor," E (exposure) is the product It^s (I = intensity, t = time of exposure and s is the Schwarzchild constant), i is the "inertia" of the plate.

To write the density numerically it is necessary to find the ratio of two blackenings. By definition $D = \log (J_0/J)$, where J_0/J is the ratio of light coming through an unblackened part of the plate to that coming through the point under consideration. The microphotometer allows this evaluation. Fig. 1 is shown as illustration. The deflection of the galvanometer of the microphotometer, a, corresponding to an unblackened part of the plate, and the null deflection, i.e., the case of no light reaching the thermo-element, are marked, respectively, as A and D. The de-

[1] D. C. Bourgin, Phys. Rev. **29**, 794 (1927).
[2] D. M. Dennison, Phys. Rev. **31**, 503 (1928).
[3] E. Bartholomé, Zeits. f. physik. Chemie **B23**, 131 (1933).
[4] G. R. Harrison, J. O. S. A. **19**, 267 (1929); L. S. Ornstein, W. J. Moll and H. C. Burger, *Objektive Spektralphotometrie* (Vieweg 1932); C. E. K. Mees, J. O. S. A. **21**, 573 (1931).

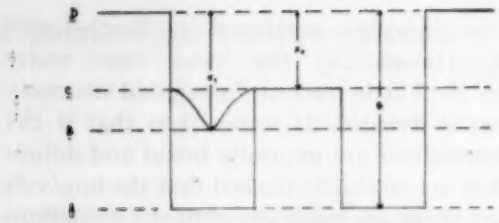

FIG. 1. *A*. Unblackened plate, i.e., complete absorption by gas. *B*. Partial absorption. *C*. Blackening by actual light source (no gas absorption). *D*. Complete blackening of photographic plate.

flections x_0, corresponding to the continuous source, and x_1, associated with a partial absorption, are shown at *C* and *B*, respectively. It may be assumed that small galvanometer deflections are proportional to the intensities of light incident on the thermopile of the microphotometer. Hence $J_0/J=a/x_0$ for the negative blackened by unabsorbed radiation from the continuous source, and $J_0/J=a/x$ for an adjacent region where the light of corresponding frequency has suffered selective partial absorption in a gas chamber.

Applying the exponential absorption law, which has been considered in the preceding section, for zero gas absorption we have

$$D_0=\gamma(\log I_0 t-\log i)=\log (a/x_0);$$

for some gas absorption

$$D=\gamma(\log It-\log i)=\log (a/x).$$

Expanding D and substituting for $\log I_0$, we get

$$\mu(\nu)N=(1/0.43\gamma)\log (x/x_0),$$

provided x and x_0 both correspond to the straight line portion of the characteristic curve. The relation is not valid when x approaches complete absorption nor when x_0 is too small resulting from overexposure of the continuous source.

What is desired is to compare $N_\nu\mu(\nu)$ for two different ν's having in general a different number of absorbing molecules N_ν, where N_ν varies with temperature. For the frequencies ν_1, ν_2

$$(\mu N)_{\nu_2}/(\mu N)_{\nu_1}=\log (x_2/x_0)/\log (x_1/x_0).$$

If ν_1 and ν_2 show fairly weak absorption so that x_2/x_0 and x_1/x_0 are both not much greater than unity** then approximately

$$(\mu N)_{\nu_2}/(\mu N)_{\nu_1}=(x_2-x_0)/(x_1-x_0)=\rho.$$

If the temperature is varied by amounts which are small compared with the absolute temperature, the approximation is allowable.

POPULATION CONSIDERATIONS

Having seen the expression for the ratio of the absorption coefficients for two frequencies, now let us see what relation holds for a band envelope absorption at two temperatures. The relative absorptions of band lines depend on the relative populations of their initial states and on relative transition probabilities. The populations of the various states are given by the distribution law

$$N_1=(p_1/p_0)N_0e^{-Ghc/kT},$$

where N_0 is the number of molecules in the normal state and G is the energy in cm^{-1} of the state whose population N_1 is under consideration; p_0 and p_1 are the statistical weights, respectively. In the case that all vibrational levels are non-degenerate (as, e.g., with non-linear triatomic molecules), and if we are dealing with unresolved bands, so that N_0, N_1 stand for the total numbers of molecules in all the rotational levels of a given vibrational level, we may put $p_1=p_0$. Changes of N_1 with temperature allow the evaluation of G, and the problem is to determine these changes from the observed changes in intensity of absorption of the vibration bands.

Curtis and Darbyshire[5] in their work on the vibrational levels of the ICl molecule call attention to the importance of the changes of N_0 with temperature, which change had been neglected by previous workers. To avoid this difficulty they worked at constant pressure and arranged conditions to obtain equality of absorption for a particular band progression at two temperatures using the change of vapor density with temperature. In the present method this matter is taken care of in the computation rather than by an experimental procedure and so avoids the difficulties of adjustment associated with a null method. For in general comparing the intensities of two bands with initial states of energy (in cm^{-1}) G_a'' and G_b'', respectively, at the

** In the expansion $e^y=1+y+\cdots$, if $y<<1$, then $\log e^y=e^y-1$, approximately.

[5] W. E. Curtis and O. Darbyshire, Trans. Faraday Soc. 27, 77 (1931).

absolute temperatures T_1 and T_2, we have

$$R_a^{(1)} = N_a^{(T_1)}/N_0^{(T_1)} = e^{-G_a'' hc/kT_1},$$

$$R_a^{(2)} = e^{-G_a'' hc/kT_2},$$

$$R_b^{(1)} = e^{-G_b'' hc/kT_1}, \quad R_b^{(2)} = e^{-G_b'' hc/kT_2}.$$

Let G_b'' be greater than G_a'' and T_2 greater than T_1. The heights of the absorption peaks will be represented by $x_a^{(T_1)}$, $x_a^{(T_2)}$, $x_b^{(T_1)}$, $x_b^{(T_2)}$ and the backgrounds corresponding to zero absorption of the continuous source $x_0^{(T_1)}$, $x_0^{(T_2)}$. The differences $x_a^{(T_1)} - x_0^{(T_1)}$, etc., are proportional then to the relative numbers of absorbing molecules.

$$\frac{R_a^{(2)}}{R_a^{(1)}} = \frac{x_a^{(T_1)} - x_0^{(T_2)}}{x_a^{(T_1)} - x_0^{(T_1)}} = \rho_a = e^{-(G_a'' hc/k)(1/T_2 - 1/T_1)},$$

$$\frac{R_b^{(2)}}{R_b^{(1)}} = \rho_b = e^{-(G_b'' hc/k)(1/T_2 - 1/T_1)},$$

$$\rho_b/\rho_a = e^{-(hc/k)(1/T_2 - 1/T_1)(G_b - G_a)''},$$

or

$$\log_{10} \rho_b/\rho_a = -0.623(1/T_2 - 1/T_1)(G_b - G_a)''.$$

That is, the differences of energy (in cm^{-1}) of the initial levels of the bands appear, so that the method may be applied to a group of bands at a time. Of the group, one is arbitrarily chosen for reference and the differences in energies between the initial levels of the other bands and that of the fiducial band can be computed. This is particularly valuable in studying bands coming from the higher initial levels, where the populations fall off rapidly with vibrational quantum number so that only part of the band system appears favorably on the photograph for a given pressure of gas in the absorption chamber. It is also convenient if a prism spectrograph with changing dispersion is used. Corrections between bands in different groups can then be determined by using exposures showing overlapping of adjoining groups. The case $G_a'' = 0$ is an important special case in the above.

Practical Considerations

Some fluctuation of the continuous source obviously is not of serious consequence in the two temperature pictures if the exposures are taken on the same plate and developed together with constant rocking. This procedure ensures that γ may be cancelled out in the computation as has been done above. According to Mees,[4] γ should be about $0.8\gamma_\infty$ for photometric work. For the galvanometer of the microphotometer to give large differences in deflection, the plate must not be very dense. Hence a shorter exposure and more prolonged development than is usual in spectroscopic work is indicated. Of course all plate blackenings must be on the straight part of the characteristic curve. Plates of medium speed are the most suitable giving a balance among latitude, contrast, speed and grain.

A small disturbance of the optical system between the two temperature exposures also does not invalidate the results obtained from the equation developed, inasmuch as a ratio of peak heights on the microphotometer traces is used. Likewise if between runs the microphotometer lamp changes slightly no serious damage is done although the lamp must remain constant during the course of any single run. However, if a long absorption tube is used, the light beam in the tube should be well collimated, since otherwise the change of refractive index of the gas with temperature will alter the cone of light so that the two plates may be of considerably different density. The optical arrangement may consist of a point source and an achromatic lens, or in the ultraviolet a long small bore hydrogen discharge tube used without a lens and with shields to limit the beam is quite satisfactory. If the intensity is sufficient, it is convenient to use no lens to focus the light emerging from the absorption chamber on the slit of the spectograph; if the light must be conserved an achromatic lens may be inserted to converge, but not focus it, in order that the spectrum shall be uniform across the slit.

Unfortunately in general the formula cannot be applied in a simple way over the whole band system due to overlapping of bands. In polyatomic spectra the complication that the band envelopes under investigation are the resultants of more or less closely overlapping vibration-rotation bands is common. Under this condition the ratios of intensities found for the absorption peaks will give apparent values of $(G_b - G_a)''$ as intermediate values which will depend on the relative strengths of the overlapping components. Nevertheless in some part of the spectrum a

group of more or less unmixed peaks is likely to be found giving a clue to the proper assignment of the bands. Then the intermediate values of $(G_b - G_a)''$ serve as intensity checks on a proposed analysis.

If there exists a background of absorption from many unresolved weak bands or a continuous background which suffers temperature variation, only an examination leading to qualitative results may be feasible. Under such circumstances the line from which peak heights in the traces are measured (x_0) will have to be drawn from an appraisal of the condition present.

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On the Absorption Spectrum of Sulphur Dioxide

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An attempt to organize the absorption bands of sulphur dioxide in the region 3900–2600A has been made. The $(000)'' - (000)'$ transition λ3129.5A (31,945 cm^{-1}) has been definitely located from a study of the temperature behavior of the lower frequency bands. Two of the vibrational frequencies known in the normal state have been observed and the intervals between successive lower levels determined. One of the frequencies in the excited state has been definitely assigned and a tentative value has been assigned for a second frequency. The configuration of the excited molecule is discussed.

INTRODUCTION

THE spectrum of sulphur dioxide, a molecule known from its permanent dipole moment to be of triangular form[1] has attracted much attention. The normal modes of vibration of this type of molecule are well known.[2] If, as is very likely true of SO_2, the strong forces are those binding two atoms (here O) to a central atom (here S), the three frequencies can be classified as ν_2, a "deformation" frequency and ν_1 and ν_3, the symmetrical and unsymmetrical "valence" frequencies. The normal state of sulphur dioxide has been investigated from infrared and Raman data and the frequencies of the normal vibrations established with some certainty.[3]

Bands involving electronic transitions occur in the ultraviolet region of the spectrum and have been recognized as jumps to more than one excited electronic state. The more intensely absorbing higher frequency band system has been examined in emission and absorption by Chow,[4] in absorption by Jonescu[5] and at still higher frequencies by Wieland.[6] The lower frequency region, which is the subject of the present communication, has already been studied by Watson and Parker,[7] who arranged some of the observed absorption bands into series. These workers however used the older frequency for the ν_2 vibration of the molecule in the normal state; also they followed the formula for a diatomic molecule separately for the three modes of vibration, as has been pointed out by Dutta.[8] It thus seemed desirable to reexamine this portion of the spectrum. As a result of the present work, the $(0, 0, 0)'' - (0, 0, 0)'$ band** has been located through detailed study of the temperature behavior of the various bands, using photo-

[1] H. A. Stuart, Zeits. f. Physik. **59**, 13 (1929).
[2] D. M. Dennison, Rev. Mod. Phys. **3**, 180 (1931).
[3] For references see H. A. Stuart, *Molekulstruktur*, Springer, 1934.
[4] T. C. Chow, Phys. Rev. **44**, 638 (1933).
[5] A. Jonescu, Comptes rendus **197**, 35 (1933).
[6] K. Wieland, Nature **130**, 847 (1932).
[7] W. W. Watson and A. E. Parker, Phys. Rev. **37**, 1484 (1931).
[8] A. K. Dutta, Acad. Sci. U. P. India Bull. **1**, 89 (1931–32).

** A level of a molecule with three normal modes of vibration must be identified by three quantum numbers. These will be given in the order v_1, v_2, v_3, and that they belong to the excited or normal electronic state will be indicated by the prime and double prime, respectively.

graphs at various pressures, and a new analysis of the system is here proposed.

The present analysis has been facilitated by several recent developments. For one thing, the intensity problem for electronic-vibrational bands of the XY_2 type of molecule has been attacked by consideration of the extended Franck-Condon principle in the case of chlorine dioxide by Urey and Johnston[9] and recently by Ku.[10] Also, applications of the group theory[11] have led to the formulation of vibrational and electronic selection rules.

Experimental

Absorption spectra were taken with various tube lengths from 40 cm to 4 meters and pressures between 1 mm and 60 cm of mercury. A 40 cm tube with 1 mm pressure brought out the bands in the region 2900A while the 4 meter tube with 60 cm pressure was required for bands at 3900A. This intensity factor of several thousand necessitated the taking of a large number of plates. The light source was a continuous hydrogen discharge for the shorter wavelengths and a tungsten filament lamp in the longer wavelength region where the lines in the hydrogen source became troublesome. Many comparison pictures with the gas at two temperatures were taken in order to be able to assign with some assurance the lower vibrational states involved in the various transitions (see below). The temperature differences were usually about 40°C, spaced about room temperature, although some plates for ranges from −80°C to 600°C were taken. The instrument used was a Hilger E3 spectrograph which was well suited to the examination of the vibrational structure, inasmuch as plates taken in the first order of the 21-foot grating showed resolution insufficient to be of additional help.

On the plates the bands obtained were so broad as to render wavelength determinations with a comparator in the usual way liable to considerable error unless many re-settings were made. To avoid this necessity, the measurements were taken from microphotometer traces, which shaped the bands and further showed up "satellite peaks" difficult to measure directly. The traces gave also the comparison of intensities required for temperature variation information. In the absence of sharp edges, wavelength determinations were made of the points of maximum absorption for each peak. Lines or the edges of opaque paper strips gummed on the plate were used as reference marks, and the intervals between then were calibrated from the iron comparison spectrum by comparator measurements. The absorption peaks measured with a scale from the reference marks on the trace were then located on the calibration "distance-wavelength" chart. Such a graph was made for each plate as the dispersion was never exactly repeated in two exposures. A large number of plates under various conditions of exposure were measured and the frequencies taken from weighted averages; except where noted each value comes from three or more plates. The uncertainty with this procedure arises from averaging values for peaks resolved on one plate with values for the same peaks only partially resolved on other plates taken under slightly different pressures. However the values were consistent within about 15 cm^{-1}.

Intensity and Temperature Variation

The use of the microphotometer as applied to the measurement of intensity changes with temperature in temperature variation of absorption spectra is discussed in the preceding paper.[12] Some of the complications encountered in practice have been more fully considered there. These may be summarized as unresolved rotational structure, overlapping of vibrational bands and the background of absorption arising from many weak bands. In spite of these embarrassments, temperature variation gave valuable clues to an arrangement of the band system.

In a gas whose molecules have only non-degenerate vibrational energy levels, the molecules are distributed among the latter according to the Boltzmann law $N_G = N_0 e^{-G''hc/kT}$. A temperature difference of 40°C is ample to show pronounced changes in intensities of absorption for bands in the spectrum of SO_2 coming from

[9] H. C. Urey and H. Johnston, Phys. Rev. **38**, 2131 (1931).
[10] Z. W. Ku, Phys. Rev. **44**, 376 (1933); **44**, 383 (1933).
[11] R. S. Mulliken, Phys. Rev. **43**, 279 (1933); L. Tisza, Zeits. f. Physik **82**, 48 (1933); A. V. Bushkovitch, Phys. Rev. **45**, 545 (1934).
[12] J. H. Clements, Phys. Rev. **47**, 220 (1935).

TABLE I. *Observed bands.*

ν	Intensity	$(G_b-G_a)''$ from Temp. Var.		ν	Intensity	$(G_b-G_a)''$ from Temp. Var.		ν	Intensity	$(G_b-G_a)''$ from Temp. Var.		ν	Intensity	$(G_b-G_a)''$ from Temp. Var.
25188	0.02			29832	.9	0		31567	60			35168	800	0
25733	.1	230		29896	.9	500		31607‡				35297 *R*	1500	
26109	.2	140		29946	1.4	0←		31646	120	500	(4)	35390		
26253*				29967	1.2	500		31719	100			35474 *S*	1200	
26469	.1	220		29994	1.2	1000		31767	80			35507 *T*	1200	
26609*				30048	1.2	1000	(2)	31793‡				35532°		
26672	.3	60		30076	1.5	0		31858	90			35634	300	
27005	.4	0←		30103	1.6	0		31926	200	200		35682	700	
27355	.1	120		30139	3.0	0		31945 *A*▪		0† ←	(5)	35742 *U*	1500	
27510	.2	200		30185	2	500		32161 *B*[L]	300			35839 *V*	1200	
27594	.2	300		30267	3	150		32377 *C*	600			35960 *W*	1000	
27940	.2	250		30343‡				32607 *D*	800			36064 *X*	600	
28200‡				30368	6	300		32850 *E*	1200			36153 *Y*	600	
28296	.3	200	(1)	30394‡				33080 *F*	1700			36241**	200	
28466	.1	400		30432‡				33313 *G*	2000			36292	500	
28514	.1	400		30500	8	200		33547 *H*	1900			36337	600	
28588	.2	550		30582	10	70		33760 *J*	2000			36381	600	
28604*	.2			30675	15	50		33960 *K*	1700			36511	500	
28802‡				30700‡				34030 *L*	1600			36558	800	
28818	.2	150		30721°	20	0←		34180 *M*	1600			36653	200	
28910*				30779‡			(3)	34200 *M'*	1600			36707		
29036	.3	400		30801‡				34241	700			36761		
29095	.2	400		30855	25	60		34396 *N*	1600			36875		
29223	.2	470		30895‡				34462 *N'*	900			36937		
29300	.2			30970	40	40		34488	400			37015		
29403	.2	400		30985‡				34620 *O*	1700			37135		
29447	.3	200		31028	40	40		34698	400			37233	600	
29472*				31065°				34724	200			37358		
29522	.3			31124	40	0		34785	1000			37442		
29622	.3			31241‡				34846 *P*	1600			37560		
29656	.5			31280‡				34940*	100			37682		
29692	.6			31330	50	0		34970	500			37773	300	
29742	.8			31360‡				35053 *Q*	1800			37810		
29798‡				31427	60	500		35133°				37900		
				31507	65									

* Indicates that the measurement is considered less reliable than the others. In most cases it comes from fewer than three plates but in others the overlapping of bands gives rise to the uncertainty.

** From this point the bands tend to become diffuse.

‡ Values taken from Watson and Parker's tables.[7] Bands not observed or not sufficiently resolved for measurement on the present writer's plates. These fit in the proposed scheme as originating from excited vibrational states and so would show more prominently on plates taken at temperatures higher than have been used here.

▪ Value taken from Lotmar's[12] series. Not clearly resolved on the present writer's plates.

[L] The letters correspond to those identifying the peaks in the reproduced microphotometer trace.

The brackets embrace the bands considered in the various temperature variation groups. For each group the arbitrarily selected fiducial band is indicated ←. (See text). For bands to the higher frequency side of † no significant variation with temperature was found.

different initial levels. With any given tube length and pressure only a small group of bands out of the whole system appears favorably. Hence selecting an arbitrary band (a), the difference between the initial level of any other band (b) of the group and that of the selected band (a) is given by the relation:

$$\log_{10}(\rho_b/\rho_a) = -0.623(1/T_2-1/T_1)(G_b-G_a)'', \quad (1)$$

where the G's are vibrational term values in cm^{-1} and ρ_b/ρ_a is the ratio on the traces of the heights of absorption peaks under examination above the line of zero absorption for the two temperatures.[12] The relation is valid only for small absorptions and a not overexposed continuous background.

As seen in Table I, temperature variation was considered in the five bracketed groups; for each group the arbitrarily selected fiducial band is indicated. To obtain reliable estimates of $(G_b-G_a)''$ it is important that the intensity range be not too great. The breaks between the groups are associated with somewhat sudden changes in the intensities, so that to relate the lower levels of the selected bands with overlapping spectrum photographs would require temperature variation comparison beyond the limits imposed in developing Eq. (1). Moreover very little confidence can be placed in the data obtained by comparing temperature variations of a band appearing at the end of one group and appearing at the beginning of the next. For in the first group the band appears with high and in the other with low intensity inasmuch as the exposure times for the two photographs are different.

For the group (4) just to the red of that showing no significant variation with temperature, the equation:

$$\log_{10}\rho_b = -0.623(1/T_2-1/T_1)G_b'' \quad (2)$$

[12] W. Lotmar, Zeits. f. Physik **83**, 765 (1933).

was used to determine directly the term values G_b'' involved. This equation is developed in the same way as Eq. (1), except that the approximation $N_0^{(T_1)} = N_0^{(T_2)}$ is made for the small temperature change. Two of the stronger absorptions showed $G_b'' = 500$ cm^{-1}, so these were assigned as coming from $(0, 1, 0)''$.

An analysis of the band system must yield an arrangement in which the frequencies in the energy level diagram, the intensities of the transitions and the temperature behavior of the bands are consistent. The vibrational levels of the normal state are known to be spaced approximately according to multiples of 500 and 1100 cm^{-1}. If for a certain peak $(G_b - G_a)''$ comes out not a multiple of 500 or 1100 but as an intermediate value when an observed ρ_b/ρ_a is substituted in Eq. (1), it may be assigned to a suitable combination of overlapping components. For example, peak A (see microphotometer trace Fig. 1) gives $(G_b - G_a)''$ as 200 cm^{-1}, which has been interpreted (see Table III) as a not too close overlapping of transitions from $(0, 0, 0)''$, $(0, 3, 0)''$, and $(1, 0, 0)''$; further overlapping components are thought to be weak. When two bands, whose spectral frequencies suggest that they be assigned as coming from the same lower level, show a small difference in temperature behavior, it is assumed that one of them is composite and it is assigned a second time in the matrix diagram of bands in the place that this difference and the intensity seem to warrant.

Theory

Any organization of the data must conform to the following theoretical demands.

(a) Group Theory[11]

The normal electronic state of this molecule of symmetry type C_{2v} may be safely assumed to be of type $^1A_1$, since SO_2 gas is diamagnetic. The excited electron state may then be A_1, B_1 or B_2, since only A_2 is forbidden to combine with A_1 according to electronic selection rules; however, weak transitions even to A_2 are possible if allowed by electronic × vibrational selection rules.[14] The normal modes of vibration ν_1, ν_2 and all resulting vibrational levels are of type a_1, while ν_3 is of type a_1 for v_3 even and b_2 for v_3 odd. The types of allowed transition will be summarized in tabular form taking the lower electronic state to be of type A_1. It will be noted that the capital letters refer to electronic types while the small letters are used to denote vibrational types. The absorption should be strong when both the electronic types and resultant electronic × vibration types are permitted by the group theory selection rules to combine. All selection rules developed will be strict even in the region of large vibrational quantum numbers, for the correction terms added to the representations of the vibrational motion to admit finite amplitudes must be of the same symmetry as those of the main term.

Table II. *Allowed transitions. Lower electronic state A_1.*

	v_3'' even		v_3'' odd	
Upper electron state	v_3' even	v_3' odd	v_3' even	v_3' odd
A_1	z	y	y	z
A_2	—	(x)	(x)	—
B_1	x	—	—	x
B_2	y	z	z	y

The letter indicates the direction of vibration associated with the electric moment in the transition; z is the symmetry axis passing through the sulphur atom in the plane of the molecule, while x is the axis at right angles to this plane. The bracket indicates that the electronic change is forbidden.

If the configuration of the molecule in the normal state is an obtuse angled triangle,[3] the moments of inertia lie $I_z > I_x > I_y$, and remain in this order for apex angle 70–180°, so that the band structures should show differences for (y) and (z). An investigation of the rotational structure under high dispersion would be necessary to show the type of excited electronic state present.

(b)

In accordance with the Franck-Condon principle the two symmetrical frequencies would be expected to appear with greater or less intensity depending on the forms of ν_1 and ν_2 and the configuration of the molecule in the excited state. If the S−O force is approximately central in nature and the S−O distance does not change very greatly during the electronic transition, the value of ν_1' should be of the same order of magnitude as ν_1''. A series with frequency differences

[14] G. Herzberg and E. Teller, Zeits. f. physik. Chemie **B21**, 410 (1933).

very much less than this would then undoubtedly be a v_2' progression.

Lower Frequency Bands

The temperature variation method points to a weak band at about 31,950 cm^{-1} as most probably the $(0, 0, 0)'' - (0, 0, 0)'$ transition. However, other possibilities not convincingly ruled out on this score were tried as origin. The choice of 31,945 cm^{-1} gave a scheme so much more consistent and in accord with intensity and temperature behavior data that there can be little doubt of its correctness. Further, the fact that it fits in with a simple-appearing series of increasing intensity lends the assignment strong support.

On the basis of this assignment of origin, vibrational quantum numbers have been assigned for a large number of the prominent bands. These are given in the form of a matrix (Table III). The averages of the differences $\Delta G_2''$ between the v_2'' levels as taken from this table run 520 cm^{-1}, 525, 529, 530, 524, 522, 511, 526, 507 cm^{-1}, the latter two values appearing from only two

TABLE III. *Lower frequency bands.*

$(v_1v_2v_3)'$ / $(v_1v_2v_3)''$	000		010		020		030		040		050		060		070		080		090	Av.
000	31945	216	32161	216	32377	230	32607	243	32850	230	33088	225	33313	234	33547	213	33760	230	33990	
	518		515		519															518
010	31427	219	31646	212	31858	Masked by strong (ono)′ progression														
	532		522		528															527
020	30895*	229	31124	206	31330	237	31567	234	31801*											
	527		542		529		528		521											529
030	30368	214	30582	219	30801*	238	31029	241	31280	227	31507	212	31719	226	31945					
	534		534		539		539		539		537				518					534
040	29832	216	30048	219	30267	233	30500	241	30741	229	30970				31427					
	532		526		522		533				538				532					530
050	29300	222	39522	220	29742	225	29967				30432*	243	30675	220	30895*					
	498				519		521				536		536							522
060	28802*				29223	223	29446	246	29692	204	29896	243	30139							
	506						536				493		518							513
070	28296						28910				29403	218	29621*							
													526							526
080													29095							
													507							507
090													28588	230	28818	218	29036			
Av.		219		215		231		241		223		228		226		216		230		
100	30801*	227	31028	213	31241*				31707	219	31926	235	32161	216	32377	230	32607	243	32850	
	534		528		520						499		515		519					519
110	30267	233	30500	221	30721	240	30961				31427	219	31646	212	31858					
	525		533		536		529				532		522		498					525
120	29742	225	29967	218	30185	247	30432*	243	30675	220	30895*	229	31124	236	31360*	207	31567	200	31767	
	519		520		529		536		536		527		542							530
130	29223	224	29447	209	29656	240	29896	243	30139	229	30368	214	30582							
											546		506							526
140											29822	254	30076							
											522									522
150											29300									
Av.		227		215		242		243		223		230		221		218		221		
200	29621*	211	29832	216	30048	219	30267	233	30500	241	30741	229	30970							
			532		526		525		506				538							525
210			29300	222	29522	220	29742	252	29994				30432*				30855	210	31065	
			498						522				536							519
220	28588	214	28802						29472	220	29692	204	29896	207	30103					
			506												541					524
230			28296												29562	236	29798*			
															526					526
240	27510										28604	214	28818	218	29036					
	505												522							514
250	27005												28296	218	28514					
	536																			536
260	26469																			
Av.		213		219		220		242		230		216		214		236		210		
500	26253	216	26469	203	26672															
	520																			520
510	25733																			
	545																			545
520	25188																			
Grand Average		220		215		232		242		224		226		219		226		221		

Nine other observed frequencies have been fitted into the scheme in scattered places conforming with the general parabolic arrangement of intensity.

* indicates a value taken from Watson and Parker's data.[2]

pairs of bands. These may be summarized by the equation

$$G_2'' = 516.4v_2'' + 4v_2''^2 - 0.4v_2''^3.$$

The occurrence of series in which the ΔG's first increase, then decrease, is not unusual in polyatomic molecules.[9] For v_1'', the ΔG's obtained vary more widely, being 1144 cm^{-1}, 1195, 1157, 1111, 1102 cm^{-1}; they follow the formula

$$G_1'' = 1086v_1'' + 70v_1''^2 - 13v_1''^3.$$

The unsymmetrical frequency known in the normal state, $\nu_3'' = 1360$ cm^{-1}, has not been mentioned in the tabular analysis. Since the band system is of considerable intensity the possibility of the excited state being of type A_2 is excluded, and the $(v_3''=0,\ v_3'=0)$ quantum jump should appear in the spectrum. Unless $\nu_3' \approx \nu_3''$, in which case $\Delta v_3 = 0$ is the most probable transition, transitions from excited unsymmetrical levels are to be expected among the lower frequency bands. The small frequency (see later) makes it probable that such bands are masked by overlapping; that is, if $(v_3'' - v_3')$ are approximately multiples of 225 cm^{-1}, the symmetrical and unsymmetrical progressions lie superposed. In an arrangement of the band system it would have been plausible to have assumed, for example, band 30,801 cm^{-1} as $(0, 0, 1)'' - (0, 0, 1)'$. However in view of the fact that the electronic type of the excited state, hence the selection rule for transition between unsymmetrical term values (see Table II), is unknown, any assignment in this way was felt would be purely arbitrary. The data for the vibrational levels of the normal state are collected in Table IV.

Table IV is of interest particularly with regard to the v_2'' series. Lotmar's values from fluorescence have very small second differences, and that the differences obtained by other workers show variation may perhaps be accounted for on the basis of band structure. It will be noted that Chow's emission values decrease with increasing quantum number, while the values in absorption run larger. That is, in emission we must say that the point of maximum intensity in the rotation band is distant from its origin by an amount which varies from band to band. In absorption the point of maximum absorption should also vary, only in this case the variation might be in the opposite direction.

TABLE IV. *Vibrational levels of the normal state.*

	Level	Infrared[9]	Chow[15]	Lotmar[15]	Jonescu‡	Present writer
v_1''	0	0	0	0	0	0
	1	1152	1150 (A)	1150	(1144)	1144
	2		2300 (A)	2300	(2270)	2339
	3		3450	3450	(3378)	3496
	4		4600	4600	(4468)	4607
	5			5750	(5540)	5709
	6			6900		
v_2''	0	0	0	0	0	0
	1	525	521	520	(530)	520
	2		1043	1040	(1060)	1045
	3		1553 (A)	1560	(1590)	1574
	4		2069	2075	(2120)	2104
	5		2578	2590	(2560)	2638
	6		3086	3110	(3180)	3150
	7		3590	3630	(3710)	3661
	8		4093			
v_3''	0	0	0	0	0	0
	1	1361	1354?	1370	(1360)	
	2		2676?	2720	(2702)	
	3		3966?	4060	(4024)	

‡ Computed from the Deslandres' formulae given.

HIGHER FREQUENCY BANDS

While the bands on the lower frequency side of the origin fall into the matrices shown in Table III, those on the higher frequency side, with the exception of the first eight members, present a confused and irregular appearance (see Fig. 1—sample microphotometer trace). Since the frequencies cannot be made to follow regular progressions, partly because the values are taken for the points of maximum absorption in each band, but perhaps mainly because of some inherent disturbances in the levels of the upper state, the microphotometer trace was examined for clues to an organization. It will be seen in Fig. 1 that the intensity increases to peak *G*, then follows a plateau of intense peaks, after which comes a somewhat regular decrease of intensity in the neighborhood of *V*. Finally appears a region of collision predissociation about 2600A, which has been explained as pressure broadening due to an influence of the existence of neighboring electron states.[16] This predissociation occurs only when selection rules are broken down by collision. The perturbing influence of the discrete levels of these same, or other, states may perhaps

[15] The summary of Chow and Lotmar's values is taken from H. D. Smyth, Phys. Rev. **44**, 690 (1933).

[16] J. Franck, H. Sponer and E. Teller, Zeits. f. physik. Chemie **B18**, 88 (1932).

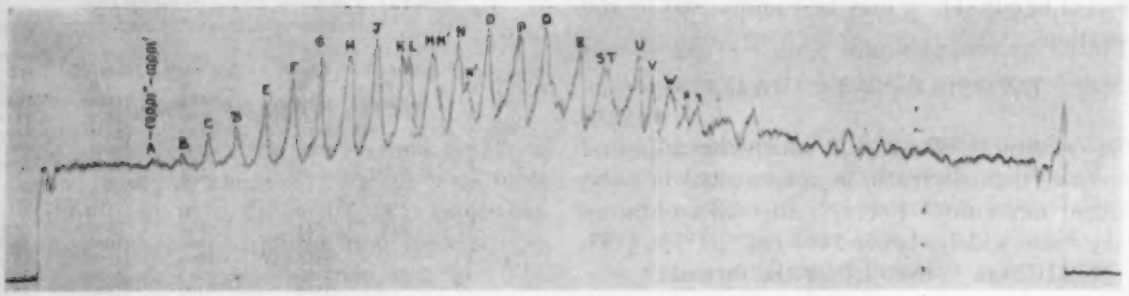

FIG. 1. Microphotometer trace of higher frequency bands. (Many lower frequency bands appear to the left of $(0, 0, 0)''-(0, 0, 0)'$ with larger numbers of molecules in the absorption path.)

be invoked to explain the irregularities among the lower frequency bands.

The plateau of intensity suggests the overlapping of a number of series of about equal intensities. In looking for the beginning of the $(1, v_2, 0)'$ progression the double peak KL is first arresting; but that the doubling indicates the first member of this progression is little likely in that the frequency interval, 2045 cm^{-1}, is somewhat larger than expected. Also the unsymmetrical appearance of peak H argues that the new series begins at lower frequency. Particularly striking also is the intense band O which is apparently rather free of satellite peaks. The appearance of the fairly intense peak V, obviously in a new series without distinct previous members, is also interesting. These observations have led to the placing of the beginning of the new progression at G (see Table V).

As in the series beginning with A, the intensity may be assumed to rise slowly, G being affected negligibly, H and J with increasing influence with the maximum of intensity at the sixth member O, corresponding to the most intense sixth member G in the $(0, v_2, 0)'$ sequence. If this has been correctly placed, the $(2, v_2, 0)'$ progression begins with O and the $(3, v_2, 0)'$ progression with V. The v_1' levels on this analysis converge rapidly and there is obviously some disturbance in the spectrum at peak O (indicated by the line drawn in Table V), which, however, is to be expected in any organization in view of the different appearance of satellites in the bands on the two sides of O. Perhaps this is due to an interaction of the normal modes of vibration in the upper states, and since v_1, v_2 and even multiples of v_3 belong to the same representation of the symmetry group, such an interaction is not improbable. If this is the case, the scheme drawn up is simply an attempt to approximately separate v_1' and v_2'. With increasing amplitudes of vibration of the molecule corresponding to the higher vibrational quantum numbers, the interaction may be supposed to increase, and that a sudden increase in coupling might occur in the upper state corresponding to the energy $A-O$, should not be regarded as too strange.

The apparent disturbance at O in Table V may be explained perhaps more satisfactorily on the basis of a sharp decrease of intensity in the $(1, v_2, 0)'$ progression at $v_2'=6$. Such intensity irregularities are known in the spectra of diatomic molecules.[17] If this is the case here, the bands

TABLE V. *Proposed transitions from (0,0,0)''.*

	$(0,v_2,0)'$		$(1,v_2,0)'$		$(2,v_2,0)'$		$(3,v_2,0)'$
$v_2'=0$	*A* 31945	1368	*G* 33313	1307	*O* 34620	1219	*V* 35839
	216		217		226		225
1	*B* 32161	1369	*H* 33530	1316	*P* 34846	1218	*X* 36064
	216		230		207		228
2	*C* 32377	1383	*J* 33760	1293	*Q* 35053	1239	36292
	230		235		244		219
3	*D* 32607	1388	*KL* 33995	1302	*R* 35297	1214	36511
	243		220		198		196
4	*E* 32850	1365	*MM'* 34215	1280	*ST* 35495	1212	36707
	230		225		247		230
5	*F* 33080	1360	*NN'* 34440	1302	*V* 35742	1195	36937
	233		180		218		198
6	*G* 33313	1307	*O* 34620	1340	*W* 35960	1175	37135
	234		226		198		223
7	*H* 33547	1299	*P* 34846	1307	*Y* 36158	1200	37358
	213		207		223		202
8	*J* 33760	1293	*Q* 35053	1328	36381	1179	37560
	235		244				
9	*KL* 33995	1302	*R* 35297				
	220		198				
10	*MM'* 34215	1280	*ST* 35495				
	247		247				
11	*NN'* 34462	1280	*V* 35742				
	236		218				
12	34698	1262	*W* 35960				

In this table $\Delta v_2'$ differences are shown horizontally and the $\Delta v_1'$ differences vertically. The break in the frequency differences at O is discussed in the text.

[17] For example, R. W. Wood and F. W. Loomis, Phil. Mag. **6**, 231 (1928); I_2 fluorescence. R. S. Mulliken, Phys. Rev. **25**, 259 (1925); BO.

below the line in $(1, \nu_2, 0)'$ are wrongly assigned, and since peak O is without a strong satellite where $(1, 6, 0)'$ should appear, the bands O, P, Q, should be placed as belonging to the $(2, \nu_2, 0)'$ progression alone. That this is the more plausible assignment is substantiated by the fact that peak V, $(3, 0, 0)'$, is much the strongest member of the $(3, \nu_2, 0)'$ progression, and thus the $(2, \nu_2, 0)'$ progression may well have a first member with relatively high transition probability.

The first few ν_2' levels should in any case not be of mixed type and their intervals appear in Table III. These levels may be represented by the formula

$$G_2' = 219\nu_2' + 1.0\nu_2'^2 + 0.5\nu_2'^3,$$

which however fails to take into account the small decrease in the difference between the second and third levels. The ν_2' frequency difference, approximately 225 cm^{-1}, as already noted by Lowater[18] is prominent throughout the band system. The ν_1' levels, if the assignment of bands just given is correct, may be approximately summarized

$$G_1' = 1373\nu_1' - 7\nu_1'^2 - 6\nu_1'^3.$$

No bands corresponding to transitions from excited vibrational levels of the normal state to levels of the excited state involving ν_1' greater then zero have been assigned. In view of the coincidence $\nu_3'' = \nu_1'' + \nu_2'$ and the approximate coincidences $\nu_3'' \approx 6\nu_2'$, $\nu_1'' \approx 5\nu_2'$, together with the uncertainties in the frequencies due to overlapping, such a definite assignment of satellite peaks does not seem justified. No significant temperature variation of these satellite peaks has been observed; this would indicate that these are weak if this interpretation of them is correct. $(1, 0, 0)'' - (1, \nu_2, 0)'$ might show most favorably through temperature changes among the weaker bands near the origin, but it is believed that the transition probability of these in this region is small.

The double bands KL, MM' and ST with reduced intensity as compared with adjoining peaks are of interest. The doubling may be ascribed to a resonance splitting of the level due to another level in close proximity, in which case the intensity of transition would be shared. Against this assumption is the apparent absence of splitting in the neighboring levels which should also be favorably placed to show the effect. Another peculiar feature of the spectrum is the slight alternation of intensity shown in the bands A−J. This at first suggested two progressions, but if so, the two progressions could not converge to the same point. No reasonable explanation of the phenomenon has been found.

[18] F. Lowater, Astrophys. J. **31**, 311 (1910).

Configurations and Force Constants of the SO_2 Molecule

From infrared investigations Bailey and Cassie[19] conclude that the normal apex angle is 122° although their valence force assumption permits both a 60° and a 120° solution. This conclusion rests on the identification of the 1360 cm^{-1} frequency as the unsymmetrical one. In the analogous molecule, ClO_2, Ku[10] on the other hand favors the acute angled form.

Van Vleck and Cross[20] have developed a valence force solution for this type of molecule, which on a present calculation leads to values of the force constants $(S-O) = 9.8\ 10^5$ and $(O-O) = 0.42\ 10^5$ dynes/cm. Here the cross terms in the potential energy expression are neglected, although if the (O−O) force is partly central in character for SO_2 these may be of importance. However a purely central force assumption does not give a solution for the frequencies observed. The S−O distance used in the present calculation is that obtained by Wierl[21] from electron diffraction, *viz.*, 1.37A. From crystal structure data the S−O distance corresponding to a single bond should be about 1.50A, while that corresponding to a double bond should be about 1.35A. If one of the bonds is single and the other double the resultant value should be closer to the double bond distance due to the exchange energy.*

[19] C. R. Bailey and A. B. D. Cassie, Proc. Roy. Soc. London **A140**, 605 (1932).

[20] J. H. Van Vleck and P. C. Cross, J. Chem. Phys. **1**, 357 (1933).

[21] W. Wierl, Phys. Zeits. **31**, 1028 (1930).

* My thanks are due to Professor Zachariasen of this department for a discussion on this point. In his opinion also the apex angle should not be greatly different from the tetrahedral angle 125°.

If the molecule is in the normal state when it absorbs the incident light, then the transition will be strongest to the excited state for which the end-point of the vibrational motion (i.e., all the vibrational energy potential) puts the molecule in the configuration most nearly that of the normal state. The intensities in Fig. 1 and the proposed arrangement in Table V show there is no single band that may be definitely taken to be the most probable transition from $(0, 0, 0)''$. The probabilities of transition of $(v_1''-v_1')$ and $(v_2''-v_2')$ (to the extent that these may be considered unmixed ν_1 and ν_2 in the two electronic states) in combination cause a number of bands to appear with about the same intensity. If the intensity explanation of the disturbance at peak *O* is accepted, a parabola of maximum intensities can be drawn in Table V. Selecting a central value on this parabola, the excited molecule vibrating with $v_1'=1$, $v_2'=3$, $v_3'=0$ may be taken as having vibrational energy potential sufficient to put the molecule in the configuration of the vibrationless normal state. The energy difference $(1, 3, 0)'-(0, 0, 0)'$ is 2050 cm^{-1} (0.25 volt). Since the S–O distance and the OSO angle both undoubtedly change from their values in the normal electronic state, it is not possible from this data to determine the shape and dimensions of the molecule in the excited state.

Jonescu[22] from a partial rotational analysis reports the OSO angle in the excited state as 96°. With the frequencies 225 cm^{-1} and 1370 cm^{-1} recognized in the spectrum, Eq. (4) of Bailey and Cassie[23] was used to suggest a possible ν_3' frequency. The solutions are in the neighborhood of 1400 and 250 cm^{-1}; the former involving the less change from the unsymmetrical frequency in the normal state appears the more likely. If then the unsymmetrical frequencies in the two states are so nearly equal it is not surprising (see discussion earlier) that these were not identified in the spectrum.

The writer wishes to thank Professor R. S. Mulliken for the suggestion of the problem and for much help and encouragement throughout the investigation.

[22] A. Jonescu, Comptes rendus **196**, 1476 (1933).
[23] C. R. Bailey and A. B. D. Cassie, Proc. Roy. Soc. London **A137**, 630 (1932).

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The Spectra of Lead IV and Bismuth V

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Early investigations in the spectra of Pb IV by Rao and Narayan, Smith and Kishen have been extended to include 34 terms arising from the configurations $5d^{10}ns$, $5d^{10}np$, $5d^{10}nd$, $5d^{10}5f$, $5d^96s^2$, $5d^96s6p$ and $5d^96s6d$. With data by Arvidsson, Smith and the author, the region reported extends from 198 to 5005A and 79 lines have been classified. In the extension to Bi V, values have been assigned to 14 terms involving 18 lines in the region below 1487A. By a Hick's formula the value of the $5d^{10}6s\ ^2S_{0\frac{1}{2}}$ term has been computed to be 340,885 cm^{-1} for Pb IV and 451,700 cm^{-1} for Bi V, giving ionization potentials of 42.0 and 55.7 volts, respectively.

PREVIOUS investigations of Pb IV by Rao and Narayan,[1] and Smith[2] established terms arising from the configurations $5d^{10}6s$, $5d^{10}6p$, $5d^{10}7s$, $5d^{10}7p$, $5d^{10}6s$, and $5d^{10}7d$ with optional assignments for the last four configurations, these assignments being commented upon by Kishen[3] in a brief note to *Nature*. Arvidsson[4] measured the spectrum below 1440A due to transitions in the various states of ionization of Pb and accordingly classified the lines as to their states of ionization. Using these data and the measurements by Smith[5] for the region 2200 to 5005A and measurements by the author for the inter-

[1] Rao and Narayan, Zeits. f. Physik **61**, 151 (1930).
[2] Smith, Phys. Rev. **36**, 1 (1930).
[3] Kishen, Nature **130**, 739 (1932).
[4] Arvidsson, Ann. d. Physik **12**, 1 (1932).
[5] Smith, Trans. Roy. Soc. Canada **22**, 331 (1928).

TABLE I. *Term values Pb IV.*

Configuration	Symbol	J	Term value	No. of Comb.
$5d^{10}6s$	^2S	$0\frac{1}{2}$	340,885	7
$5d^{10}6p$	$^2P^o$	$0\frac{1}{2}$	264,730	6
	$^2P^o$	$1\frac{1}{2}$	243,668	8
$5d^96s^2$	^2D	$2\frac{1}{2}$	253,135	4
	^2D	$1\frac{1}{2}$	229,866	3
—	1	$2\frac{1}{2}$	250,208	7
	2	$2\frac{1}{2}$	243,533	6
	3	$2\frac{1}{2}$	239,635	3
	4	$0\frac{1}{2}$	189,198	2
$5d^96s6p$	1°	$2\frac{1}{2}$	185,239	3
	2°	$1\frac{1}{2}$	183,088	3
	3°	$2\frac{1}{2}$	179,000	4
	4°	$2\frac{1}{2}$	173,821	3
	5°	$2\frac{1}{2}$	173,222	2
$5d^{10}7s$	^2S	$0\frac{1}{2}$	155,784	8
$5d^{10}6d$	^2D	$1\frac{1}{2}$	156,328	11
	^2D	$2\frac{1}{2}$	154,070	7
$5d^96s6d$	5	$1\frac{1}{2}$	155,739	3
	6	$1\frac{1}{2}$	155,188	3
$5d^96s6p$	6°	$3\frac{1}{2}$	155,174	3
	7°	$3\frac{1}{2}$	152,581	4
	8°	$1\frac{1}{2}$	140,138	4
	9°	$1\frac{1}{2}$	131,835	11
	10°	$1\frac{1}{2}$	130,518	6
	11°	$0\frac{1}{2}$	129,667	3
	12°	$1\frac{1}{2}$	117,542	5
$5d^{10}7p$	$^2P^o$	$0\frac{1}{2}$	131,097	5
	$^2P^o$	$1\frac{1}{2}$	123,035	12
$5d^{10}5f$	$^2F^o$	$3\frac{1}{2}$	119,169	3
	$^2F^o$	$2\frac{1}{2}$	114,432	4
$5d^96s6d$	7	$3\frac{1}{2}$	101,545	4
$5d^{10}8s$	^2S	$0\frac{1}{2}$	91,251	5
$5d^{10}7d$	^2D	$1\frac{1}{2}$	90,485	9
	^2D	$2\frac{1}{2}$	89,467	7

TABLE II. *Classified lines of Pb IV.*

Measurements: 459–1438A Arvidsson[4], 1438–1960 Author, 1960–4497A Smith.[5]

C	I	λ(vac.)	ν(vac.)	Combination
4	6	459.04	217846	$5d^{10}6s\ ^2S_{\frac{1}{2}} - 5d^{10}7p\ ^2P^o_{1\frac{1}{2}}$
4	1	473.45	211216	$5d^{10}6s\ ^2S_{\frac{1}{2}} - 5d^96s6p\ 11^o_{1\frac{1}{2}}$
4	7	475.36	210367	$5d^{10}6s\ ^2S_{\frac{1}{2}} - 5d^96s6p\ 10^o_{1\frac{1}{2}}$
4	8	478.355	209050	$5d^{10}6s\ ^2S_{\frac{1}{2}} - 5d^96s6p\ 9^o_{1\frac{1}{2}}$
4	2	498.14	200747	$5d^{10}6s\ ^2S_{\frac{1}{2}} - 5d^96s6p\ 8^o_{1\frac{1}{2}}$
4	2	573.90	174246	$5d^{10}6p\ ^2P^o_{0\frac{1}{2}} - 5d^{10}7d\ ^2D_{1\frac{1}{2}}$
4	2	576.43	173482	$5d^{10}6p\ ^2P^o_{0\frac{1}{2}} - 5d^{10}8s\ ^2S_{\frac{1}{2}}$
4	2	648.50	154202	$5d^{10}6p\ ^2P^o_{1\frac{1}{2}} - 5d^{10}7d\ ^2D_{2\frac{1}{2}}$
6	3	652.81	153184	$5d^{10}6p\ ^2P^o_{1\frac{1}{2}} - 5d^{10}7d\ ^2D_{1\frac{1}{2}}$
4	2	656.09	152418	$5d^{10}6p\ ^2P^o_{1\frac{1}{2}} - 5d^{10}8s\ ^2S_{\frac{1}{2}}$
	0	829.89	120498	$2_{2\frac{1}{2}} - 5d^{10}7p\ ^2P^o_{1\frac{1}{2}}$
4	7	830.11	120466	$3_{2\frac{1}{2}} - 5d^{10}5f\ ^2F^o_{3\frac{1}{2}}$
4	2	844.79	118373	$1_{1\frac{1}{2}} - 5d^96s6p\ 9^o_{1\frac{1}{2}}$
5	7	857.65	116598	$3_{2\frac{1}{2}} - 5d^{10}7p\ ^2P^o_{1\frac{1}{2}}$
	0	866.31	115432	$5d^96s^2\ ^2D_{1\frac{1}{2}} - 5d^{10}5f\ ^2F^o_{2\frac{1}{2}}$
4	6	884.98	112997	$5d^96s^2\ ^2D_{2\frac{1}{2}} - 5d^96s6p\ 8^o_{1\frac{1}{2}}$
4	6	908.51	110070	$1_{1\frac{1}{2}} - 5d^96s6p\ 8^o_{1\frac{1}{2}}$
4	7	917.89	108946	$5d^{10}6p\ ^2P^o_{0\frac{1}{2}} - 5d^{10}7s\ ^2S_{\frac{1}{2}}$
4	10	922.49	108402	$5d^{10}6p\ ^2P^o_{0\frac{1}{2}} - 5d^{10}6d\ ^2D_{1\frac{1}{2}}$
4	7	927.62	107803	$3_{2\frac{1}{2}} - 5d^96s6p\ 9^o_{1\frac{1}{2}}$
	0	936.05	106832	$5d^96s^2\ ^2D_{1\frac{1}{2}} - 5d^{10}7p\ ^2P^o_{1\frac{1}{2}}$
4	0	967.15	103397	$2_{2\frac{1}{2}} - 5d^96s6p\ 8^o_{1\frac{1}{2}}$
	0	994.53	100550	$5d^96s^2\ ^2D_{2\frac{1}{2}} - 5d^96s6p\ 7^o_{2\frac{1}{2}}$
4	3	1012.47	98768.4	$5d^96s^2\ ^2D_{1\frac{1}{2}} - 5d^{10}7p\ ^2P^o_{0\frac{1}{2}}$
5	3	1024.33	97624.8	$1_{2\frac{1}{2}} - 5d^96s6p\ 7^o_{2\frac{1}{2}}$
4	30	1028.61	97218.6	$5d^{10}6s\ ^2S_{\frac{1}{2}} - 5d^{10}6p\ ^2P^o_{1\frac{1}{2}}$
4	3	1044.14	95772.6	$5d^96s6p\ 1^o_{2\frac{1}{2}} - 5d^{10}7d\ ^2D_{2\frac{1}{2}}$
4	4	1052.25	95034.4	$1_{2\frac{1}{2}} - 5d^96s6p\ 6^o_{2\frac{1}{2}}$
4	2	1079.88	92602.9	$5d^96s6p\ 2^o_{1\frac{1}{2}} - 5d^{10}7d\ ^2D_{1\frac{1}{2}}$
4	1	1099.46	90953.7	$2_{2\frac{1}{2}} - 5d^96s6p\ 7^o_{2\frac{1}{2}}$
4	7	1116.08	89599.3	$5d^{10}6p\ ^2P^o_{1\frac{1}{2}} - 5d^{10}6d\ ^2D_{2\frac{1}{2}}$
6	4	1131.76	88358.0	$2_{2\frac{1}{2}} - 5d^96s6p\ 6^o_{2\frac{1}{2}}$
4	7	1137.86	87884.3	$5d^{10}6p\ ^2P^o_{1\frac{1}{2}} - 5d^{10}7s\ ^2S_{\frac{1}{2}}$
4	6	1144.95	87340.1	$5d^{10}6p\ ^2P^o_{1\frac{1}{2}} - 5d^{10}6d\ ^2D_{1\frac{1}{2}}$
5	1	1260.82	79313.5	$5d^96s^2\ ^2D_{2\frac{1}{2}} - 5d^96s6p\ 4^o_{2\frac{1}{2}}$
4	2	1291.08	77454.5	$5d^96s6p\ 3^o_{2\frac{1}{2}} - 5d^96s6d\ 7_{3\frac{1}{2}}$
4	1	1298.93	76986.4	$1_{2\frac{1}{2}} - 5d^96s6p\ 5^o_{2\frac{1}{2}}$
4	0	1309.13	76386.6	$1_{2\frac{1}{2}} - 5d^96s6p\ 4^o_{2\frac{1}{2}}$
4	40	1313.06	76158.0	$5d^{10}6s\ ^2S_{\frac{1}{2}} - 5d^{10}6p\ ^2P^o_{1\frac{1}{2}}$
4	1	1323.92	75533.3	$5d^{10}6p\ ^2P^o_{0\frac{1}{2}} - 4_{0\frac{1}{2}}$
4	6	1348.87	74136.1	$5d^96s^2\ ^2D_{2\frac{1}{2}} - 5d^96s6p\ 3^o_{2\frac{1}{2}}$
4	1	1395.14	71677.4	$5d^96s6p\ 5^o_{2\frac{1}{2}} - 5d^96s6d\ 7_{3\frac{1}{2}}$
4	1	1404.34	71207.8	$1_{2\frac{1}{2}} - 5d^96s6p\ 3^o_{2\frac{1}{2}}$
4	0	1437.47	69712.2	$2_{2\frac{1}{2}} - 5d^96s6p\ 4^o_{2\frac{1}{2}}$
	1	1715.39	58295.8	$2_{2\frac{1}{2}} - 5d^96s6p\ 1^o_{2\frac{1}{2}}$
	4	1835.88	54469.8	$5d^{10}6p\ ^2P^o_{1\frac{1}{2}} - 4_{0\frac{1}{2}}$
	6	1864.47	53634.5	$5d^96s6p\ 6^o_{3\frac{1}{2}} - 5d^96s6d\ 7_{4\frac{1}{2}}$
	6	1959.42	51035.5	$5d^96s6p\ 7^o_{3\frac{1}{2}} - 5d^95s6d\ 7_{4\frac{1}{2}}$
		λ(air)		
	0	2359.55	42368.0	$5d^96s6p\ 9^o_{1\frac{1}{2}} - 5d^{10}7d\ ^2D_{2\frac{1}{2}}$
	0	2385.81	41901.7	$5d^{10}6d\ ^2D_{1\frac{1}{2}} - 5d^{10}5f\ ^2F^o_{2\frac{1}{2}}$
	00	2417.69	41349.2	$5d^96s6p\ 9^o_{2\frac{1}{2}} - 5d^{10}7d\ ^2D_{1\frac{1}{2}}$
	4	2461.51	40613.2	$5d^{10}7p\ ^2P^o_{0\frac{1}{2}} - 5d^{10}7d\ ^2D_{1\frac{1}{2}}$
	0	2463.32	40583.3	$5d^96s6p\ 9^o_{2\frac{1}{2}} - 5d^{10}8s\ ^2S_{\frac{1}{2}}$
	0	2497.17	40033.3	$5d^96s6p\ 10^o_{1\frac{1}{2}} - 5d^{10}7d\ ^2D_{1\frac{1}{2}}$
	2	2508.90	39846.1	$5d^{10}7p\ ^2P^o_{0\frac{1}{2}} - 5d^{10}8s\ ^2S_{\frac{1}{2}}$
	1	2577.30	38788.7	$5d^{10}6d\ ^2D_{1\frac{1}{2}} - 5d^96s6p\ 12^o_{1\frac{1}{2}}$
	6	2614.21	38241.1	$5d^{10}7s\ ^2S_{\frac{1}{2}} - 5d^96s6p\ 12^o_{1\frac{1}{2}}$
	00	2736.91	36526.8	$5d^{10}6d\ ^2D_{2\frac{1}{2}} - 5d^96s6p\ 12^o_{2\frac{1}{2}}$
	7	2864.26	34902.8	$5d^{10}6d\ ^2D_{2\frac{1}{2}} - 5d^{10}5f\ ^2F^o_{3\frac{1}{2}}$
	4	2978.26	33566.9	$5d^{10}7p\ ^2P^o_{1\frac{1}{2}} - 5d^{10}7d\ ^2D_{2\frac{1}{2}}$
	2	3002.78	33292.8	$5d^{10}6d\ ^2D_{1\frac{1}{2}} - 5d^{10}7p\ ^2P^o_{1\frac{1}{2}}$
	7	3052.66	32748.8	$5d^{10}7s\ ^2S_{\frac{1}{2}} - 5d^{10}7p\ ^2P^o_{1\frac{1}{2}}$
	00	3056.82	32704.3	$5d^96s6d\ 5_{3\frac{1}{2}} - 5d^{10}7p\ ^2P^o_{1\frac{1}{2}}$
	1	3071.41	32548.9	$5d^{10}7p\ ^2P^o_{1\frac{1}{2}} - 5d^{10}7d\ ^2D_{1\frac{1}{2}}$
	1	3109.23	32153.0	$5d^96s6d\ 6_{3\frac{1}{2}} - 5d^{10}7p\ ^2P^o_{1\frac{1}{2}}$
	2	3145.60	31781.3	$5d^{10}7p\ ^2P^o_{1\frac{1}{2}} - 5d^{10}8s\ ^2S_{\frac{1}{2}}$
	00	3207.47	31168.2	$5d^96s6p\ 1^o_{2\frac{1}{2}} - 5d^{10}6d\ ^2D_{2\frac{1}{2}}$
	6	3221.30	31034.4	$5d^{10}6d\ ^2D_{2\frac{1}{2}} - 5d^{10}7p\ ^2P^o_{1\frac{1}{2}}$
	2	3365.74	29702.6	$5d^{10}5f\ ^2F^o_{3\frac{1}{2}} - 5d^{10}7d\ ^2D_{2\frac{1}{2}}$
	3	3560.88	28075.0	$5d^96s6p\ 12^o_{1\frac{1}{2}} - 5d^{10}7d\ ^2D_{1\frac{1}{2}}$
	8	3655.61	27347.5	$5d^96s6p\ 2^o_{1\frac{1}{2}} - 5d^96s6d\ 5_{3\frac{1}{2}}$
	00	3694.25	27061.4	$5d^96s6p\ 12^o_{2\frac{1}{2}} - 5d^{10}7d\ ^2D_{2\frac{1}{2}}$
	5	3736.00	26759.0	$5d^96s6p\ 2^o_{2\frac{1}{2}} - 5d^{10}6d\ ^2D_{2\frac{1}{2}}$
	0	3749.15	26665.2	$5d^{10}6d\ ^2D_{1\frac{1}{2}} - 5d^96s6p\ 11^o_{2\frac{1}{2}}$
	5	3827.53	26119.1	$5d^{10}7s\ ^2S_{\frac{1}{2}} - 5d^96s6p\ 11^o_{2\frac{1}{2}}$
	0	3873.36	25810.1	$5d^{10}6d\ ^2D_{1\frac{1}{2}} - 5d^96s6p\ 10^o_{1\frac{1}{2}}$
	0	3957.26	25262.9	$5d^{10}7s\ ^2S_{\frac{1}{2}} - 5d^96s6p\ 10^o_{2\frac{1}{2}}$
	6	3962.45	25229.8	$5d^{10}6d\ ^2D_{1\frac{1}{2}} - 5d^{10}7p\ ^2P^o_{2\frac{1}{2}}$
	2	4004.16	24967.0	$5d^{10}5f\ ^2F^o_{3\frac{1}{2}} - 5d^{10}7d\ ^2D_{2\frac{1}{2}}$
	4	4049.79	24685.7	$5d^{10}7s\ ^2S_{\frac{1}{2}} - 5d^{10}7p\ ^2P^o_{2\frac{1}{2}}$
	0	4052.52	24669.1	$5d^96s6d\ 6_{3\frac{1}{2}} - 5d^96s6p\ 10^o_{1\frac{1}{2}}$
	0	4081.84	24492.9	$5d^{10}6d\ ^2D_{1\frac{1}{2}} - 5d^96s6p\ 9^o_{1\frac{1}{2}}$
	2	4174.46	23948.5	$5d^{10}7s\ ^2S_{\frac{1}{2}} - 5d^96s6p\ 9^o_{1\frac{1}{2}}$ $5d^{10}5f\ ^2F^o_{2\frac{1}{2}} - 5d^{10}7d\ ^2D_{1\frac{1}{2}}$
	5	4182.40	23903.0	$5d^96s6d\ 5_{4\frac{1}{2}} - 5d^96s6p\ 9^o_{2\frac{1}{2}}$
	10	4245.08	23550.1	$5d^{10}6d\ ^2D_{2\frac{1}{2}} - 5d^96s6p\ 10^o_{2\frac{1}{2}}$
	00	4281.25	23351.1	$5d^96s6d\ 6_{4\frac{1}{2}} - 5d^96s6p\ 9^o_{2\frac{1}{2}}$
	00	4410.18	22668.5	$5d^96s6p\ 3^o_{2\frac{1}{2}} - 5d^{10}6d\ ^2D_{1\frac{1}{2}}$
	2	4496.21	22234.7	$5d^{10}6d\ ^2D_{2\frac{1}{2}} - 5d^96s6p\ 9^o_{2\frac{1}{2}}$

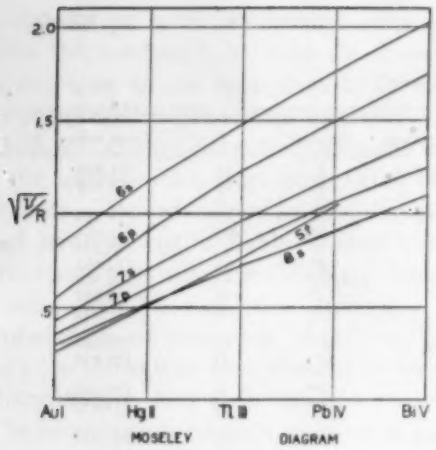

FIG. 1. Moseley diagram.

mediate region, an analysis of the spectrum of Pb IV is reported here from 198 to 5005A and values have been assigned to 34 terms which arise from the configurations $5d^{10}ns$, $5d^{10}np$, $5d^{10}nd$, $5d^{10}5f$, $5d^{9}6s^{2}$, $5d^{9}6s6p$ and $5d^{9}6s6d$. These term values, referred to $5d^{10}\,{}^{1}S_{0}$ of Pb V, are given in Table I. The 79 classified lines for Pb IV appear in Table II, where in the column C is given the classification as to the state of ionization as made by Arvidsson.

Arvidsson[4] classified three pairs of doublets in Bi V, and this report extends the classification to 18 lines, establishing 14 terms due to $5d^{10}ns$, $5d^{10}np$, $5d^{10}nd$, and $5d^{9}6s^{2}$ configurations. These term values, referred to $5d^{10}\,{}^{1}S_{0}$ of Bi VI, are given in Table III. In the present investigation the region was limited to the measurements by Arvidsson from 176 to 1487A. In Table IV are the classified lines, the column C giving Arvidsson's classification as to the state of ionization.

In the Moseley diagram, Fig. 1, curves are given for the principal terms. The absolute values have been determined by applying a Hick's formula to the $5d^{10}6s$, $5d^{10}7s$, and $5d^{10}8s$ terms in each spectrum, obtaining 340,885 cm^{-1} for the $5d^{10}6s\ {}^{2}S_{0\frac{1}{2}}$ term of Pb IV and 451,700 cm^{-1} for the corresponding term of Bi V, giving ionization potentials of 42.0 and 55.7 volts, respectively. The characteristically large hyperfine structure of Bi is noted as 13 cm^{-1} for the ${}^{2}S_{0\frac{1}{2}}$ term.

TABLE III. *Term values Bi V.*

Configuration	Symbol	J	Term value	No. of Comb.
$5d^{10}6s$	${}^{2}S$	$0\frac{1}{2}$	451,700 *h*	4
$5d^{10}6p$	${}^{2}P^{o}$	$0\frac{1}{2}$	363,940	6
	${}^{2}P^{o}$	$1\frac{1}{2}$	336,019	7
$5d^{9}6s^{2}$	${}^{2}D$	$2\frac{1}{2}$	348,044	1
	${}^{2}D$	$1\frac{1}{2}$	317,928	2
—	1	$1\frac{1}{2}$	228,470	2
$5d^{10}6d$	${}^{2}D$	$1\frac{1}{2}$	222,405	2
	${}^{2}D$	$2\frac{1}{2}$	219,153	1
$5d^{10}7s$	${}^{2}S$	$0\frac{1}{2}$	218,353	2
$5d^{10}7p$	${}^{2}P^{o}$	$0\frac{1}{2}$	181,075	2
	${}^{2}P^{o}$	$1\frac{1}{2}$	170,619	3
$5d^{10}7d$	${}^{2}D$	$1\frac{1}{2}$	134,387	1
	${}^{2}D$	$2\frac{1}{2}$	133,064	1
$5d^{10}8s$	${}^{2}S$	$0\frac{1}{2}$	131,264	2

h hyperfine separation $\Delta\nu = 13 cm^{-1}$.

TABLE IV. *Classified lines of Bi V.*

Measurements: Arvidsson.[4]

C	I	λ(vac.)	ν(vac.)	Combination
5	1	355.769	281081	$5d^{10}6s\ {}^{2}S_{0\frac{1}{2}} - 5d^{10}7p\ {}^{2}P^{o}_{1\frac{1}{2}}$
5	1	369.515	270625	$5d^{10}6s\ {}^{2}S_{0\frac{1}{2}} - 5d^{10}7p\ {}^{2}P^{o}_{0\frac{1}{2}}$
4	1	429.78	232677	$5d^{10}6p\ {}^{2}P^{o}_{0\frac{1}{2}} - 5d^{10}8s\ {}^{2}S_{0\frac{1}{2}}$
5	1	435.63	229553	$5d^{10}6p\ {}^{2}P^{o}_{0\frac{1}{2}} - 5d^{10}7d\ {}^{2}D_{1\frac{1}{2}}$
5	2	488.39	204754	$5d^{10}6p\ {}^{2}P^{o}_{1\frac{1}{2}} - 5d^{10}8s\ {}^{2}S_{0\frac{1}{2}}$
5	1	492.72	202955	$5d^{10}6p\ {}^{2}P^{o}_{1\frac{1}{2}} - 5d^{10}7d\ {}^{2}D_{2\frac{1}{2}}$
6	3	563.62	177425	$5d^{9}6s^{2}\ {}^{2}D_{2\frac{1}{2}} - 5d^{10}7p\ {}^{2}P^{o}_{1\frac{1}{2}}$
5	2	678.87	147304	$5d^{9}6s^{2}\ {}^{2}D_{1\frac{1}{2}} - 5d^{10}7p\ {}^{2}P^{o}_{1\frac{1}{2}}$
5	6	686.88	145586	$5d^{10}6p\ {}^{2}P^{o}_{0\frac{1}{2}} - 5d^{10}7s\ {}^{2}S_{0\frac{1}{2}}$
6	1	706.54	141535	$5d^{10}6p\ {}^{2}P^{o}_{0\frac{1}{2}} - 5d^{10}6d\ {}^{2}D_{1\frac{1}{2}}$
5	5	730.71	136853	$5d^{9}6s^{2}\ {}^{2}D_{1\frac{1}{2}} - 5d^{10}7p\ {}^{2}P^{o}_{0\frac{1}{2}}$
5	10	738.17	135470	$5d^{10}6p\ {}^{2}P^{o}_{0\frac{1}{2}} - 1_{1\frac{1}{2}}$
5	6	849.86	117666	$5d^{10}6p\ {}^{2}P^{o}_{1\frac{1}{2}} - 5d^{10}7s\ {}^{2}S_{0\frac{1}{2}}$
5	5	855.68	116866	$5d^{10}6p\ {}^{2}P^{o}_{1\frac{1}{2}} - 5d^{10}6d\ {}^{2}D_{2\frac{1}{2}}$
5	15	864.403	115686.8	$5d^{10}6s\ {}^{2}S_{0\frac{1}{2}} - 5d^{10}6p\ {}^{2}P^{o}_{1\frac{1}{2}}$
		0.499	115673.9	
5	6	880.17	113614	$5d^{10}6p\ {}^{2}P^{o}_{1\frac{1}{2}} - 5d^{10}6d\ {}^{2}D_{1\frac{1}{2}}$
5	6	929.81	107549	$5d^{10}6p\ {}^{2}P^{o}_{1\frac{1}{2}} - 1_{1\frac{1}{2}}$
5	15	1139.370	87767.8	$5d^{10}6s\ {}^{2}S_{0\frac{1}{2}} - 5d^{10}6p\ {}^{2}P^{o}_{0\frac{1}{2}}$
		0.548	87754.1	

Vibrations of Symmetrical Tetratomic Molecules

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The general method for obtaining the vibration frequencies of any symmetrical molecule is outlined, and the results of its application to the tetratomic case are given. The frequencies are derived for the most general force field consistent with geometrical symmetry and also for a more specific case based on a simplified model. It is shown that the assumption of the rigidity of the bonds requires two different forces perpendicular to the lines of bond. The coplanar tetratomic and the collinear triatomic molecules are found to be the only ones of a number of molecules investigated so far, where an unambiguous determination of the physical force constants is possible. In the general case, no very definite meaning can, apparently, be attached to terms like "magnitude of bond constant."

THE general procedure for obtaining the normal vibration frequencies of a molecule of any type of symmetry, with the minimum amount of calculations and without the use of group theory, may be summarized briefly in the following manner.[1] We write the expression for the kinetic energy T in terms of the displacements of the various atoms from their equilibrium positions. The potential energy, V, a function of the mutual displacements of the atoms, is written in terms of these variables as the most general quadratic form consistent with geometrical symmetry. (For small vibrations there is a linear connection between the mutual displacements of the atoms and their displacements from the positions of equilibrium.) As the next step, new variables, linear combinations of the original displacements, are introduced and both T and V are transformed to them, the usual assumptions of the conservation of the linear and angular momenta are taken into account when the transformation on T is performed. The normal vibration frequencies, ω, or rather $\lambda=4\pi^2\omega^2$, are then obtained as the roots of $|\lambda T-V|=0$. For n degrees of internal freedom, the expansion of this nth order determinant will give rise to an equation in λ of the nth degree. For molecules with some kind of symmetry, this nth degree equation may usually be resolved into a number of component equations of lesser degree. In this case, it is possible, by a proper choice of variables, to resolve the original determinant immediately into a product of determinants of lesser order. This proper choice of variables is, to some extent, a matter of guess-work in each particular case, but, they are usually indicated by the symmetry of the geometrical configuration. A fairly detailed treatment illustrating the procedure outlined here has been given for the symmetrical tetrahedral pentatomic molecules.[2] Some of the results of its application to tetratomic molecules of the type YX_3 have also been previously reported.[3, 4] A complete discussion of the vibration frequencies and isotopic shifts of tetratomic molecules, both of the pyramidal and coplanar types, will now be given together with a discussion of various intramolecular forces and of the physical meaning of the results.

Denoting, as usual, the positions of the three X atoms by A_1, A_2, A_3 and that of the Y atom by A_4, we let

$$A_4A_i=r_i=r^0+\delta r_i;\quad A_iA_j=q_{ij}=q^0+\delta q_{ij};$$

$$A_iA_4A_j=2\Omega_{ij}=2(\Omega^0+\delta\Omega_{ij});\quad (i,j=1,2,3);$$

(the superscript 0 refers to the equilibrium configuration). The δr_i and δq_{ij} are the mutual displacements of the particles. z^0 denotes the height of the pyramid and $g=z^0/q^0$,

$$r^{02}=z^{02}+\tfrac{1}{3}q^{02}=\tfrac{1}{3}q^{02}(1+3g^2).$$

We introduce:

$$x+\tfrac{1}{2}u=(\delta r_2-\delta r_3)(r^0/q^0);\quad u=\delta q_{13}-\delta q_{13};$$

$$y+\tfrac{1}{2}t=(2/\sqrt{3})[\tfrac{1}{2}(\delta r_2+\delta r_3)-\delta r_1](r^0/q^0);$$

$$t=-(2/\sqrt{3})[\tfrac{1}{2}(\delta q_{12}+\delta q_{13})-\delta q_{23}];$$

$$3gz+w/\sqrt{3}=(\delta r_1+\delta r_2+\delta r_3)(r^0/q^0);$$

$$w=(\delta q_{12}+\delta q_{13}+\delta q_{23})/\sqrt{3}. \qquad (1)$$

x, y and z may be shown to be the displacements

[1] A group-theoretical method giving qualitative but not quantitative results has been given by E. Bright Wilson, Jr., J. Chem. Phys. **2**, 432 (1934).

[2] J. E. Rosenthal, Phys. Rev. **45**, 538 (1934).

[3] E. O. Salant and J. E. Rosenthal, Phys. Rev. **42**, 812 (1932).

[4] J. E. Rosenthal, Phys. Rev. **45**, 426 (1934).

of the Y atom from its equilibrium position; x and y are parallel to the plane of the X atoms and z is perpendicular to it. With the six arbitrary constants permitted by the geometrical symmetry,[5] the potential energy, V, is written as:[6]

$$V(x,y,z,u,t,w)=\tfrac{1}{2}[A(x^2+y^2)+Bz^2+Cw^2 +D(u^2+t^2)+2E(xu+yt)+2Fzw]. \quad (2)$$

If the three X atoms have the same mass: $m_1=m_2=m_3=m$ (i.e., if we disregard isotope effects) and if M is the mass of the Y atom, the corresponding expression for the kinetic energy is

$$T=\tfrac{1}{2}m[3\mu(\dot{x}^2+\dot{y}^2)/b+3\mu\dot{z}^2+\tfrac{1}{3}(\dot{u}^2+\dot{t}^2+\dot{w}^2)], \quad (3)$$

where $\mu=M/(M+3m)$ and $b=1+6\mu g^2$.

The frequencies are then given by

$$\begin{aligned}&[m^2\lambda^2_{(xu),\,(yt)}-m\lambda(\tfrac{1}{3}Ab/\mu+3D) +(b/\mu)(AD-E^2)]^2=0,\\ &m^2\lambda^2_{(zw)}-m\lambda(\tfrac{1}{3}B/\mu+3C)+(BC-F^2)/\mu=0.\end{aligned} \quad (4)$$

The subscripts attached to λ indicate to what variables, hence to what types of motion, these frequencies correspond. With this notation it is immediately evident that the vibrations of the electric moment are parallel to the symmetry axis of the molecule for the two single frequencies represented by $\omega_{(zw)}$ and perpendicular to it for the two double frequencies.

In the case where one of the X atoms is replaced by its isotope X^* so that $m_1=m+\Delta m$, while $m_2=m_3=m$, the kinetic energy becomes:

$$\begin{aligned}T=&\tfrac{1}{2}m[b(1-\kappa)-\mu\kappa]^{-1}[3\mu(1-\kappa)\dot{x}^2\\ &+\tfrac{1}{3}(b-\mu\kappa)\dot{u}^2-2\mu\kappa\dot{u}\dot{x}]+\tfrac{1}{2}m[b'(1-2\kappa-\mu\kappa)]^{-1}\\ &\times\{3\mu(1-2\kappa)(1-\mu\kappa)\dot{y}^2+3\mu[b'(1-2\kappa)-2\mu\kappa^2]\dot{z}^2\\ &+\tfrac{1}{3}[b'(1-\kappa-\mu\kappa)-\mu\kappa^2(b-1)](\dot{t}^2+\dot{w}^2)\\ &+2[\mu\kappa(1-\mu\kappa)\dot{y}(\dot{t}-\dot{w})-6\kappa(1-2\kappa)g\mu^2\dot{y}\dot{z}\sqrt{3}\\ &-2\kappa^2\mu^2g\dot{z}(\dot{t}-\dot{w})\sqrt{3}-\tfrac{1}{3}\kappa(b'-\mu\kappa b+\mu\kappa)\dot{t}\dot{w}]\}; \quad (3')\end{aligned}$$

where $b'=b(1-2\kappa)+2\kappa-\mu\kappa$. The corresponding frequencies are given by:

$$\begin{aligned}&m^2\lambda^2-m\lambda[\tfrac{1}{3}A(b/\mu-\kappa)+3D(1-\kappa)+2\kappa E] +[(1-\kappa)b/\mu-\kappa](AD-E^2)=0, \quad (4')\\ &m^4\lambda^4_{(yt\,zw)}-P_1m^3\lambda^3+P_2m^2\lambda^2-P_3m\lambda+P_4=0,\end{aligned}$$

where:

$$\begin{aligned}P_1=&[\tfrac{1}{3}Ab'/\mu+3(1-\kappa)D-2\kappa E] +[\tfrac{1}{3}(1-\mu\kappa)B/\mu+3C(1-\kappa)];\\ P_2=&[\tfrac{1}{3}(1-\mu\kappa)B/\mu+3C(1-\kappa)][\tfrac{1}{3}Ab'/\mu\\ &+3(1-\kappa)D-2\kappa E]+(1/\mu-\kappa)(1-\kappa)(BC-F^2)\\ &+(b'/\mu)(1-\kappa)(AD-E^2)-\kappa^2[(4/3)g^2AB\\ &+AC+AD-E^2+4gF(A+3E)/\sqrt{3} +9CD+6CE];\\ P_3=&(b'/\mu)(1-\kappa)(AD-E^2)[\tfrac{1}{3}(1-\mu\kappa)B/\mu\\ &+3C(1-\kappa)]+(1/\mu)(1-\kappa)(1-\mu\kappa)(BC-F^2)\\ &\times[\tfrac{1}{3}Ab'/\mu+3D(1-\kappa)-2\kappa E]-(\kappa^2/\mu)\\ &\times\{(AD-E^2)[\tfrac{1}{3}B(b'+b-1)+3C(b'+2\mu)\\ &+4\mu gF\sqrt{3}]+(BC-F^2)[\tfrac{1}{3}A(b'+b-1)\\ &+3(1-\mu\kappa)D+2(1-\mu\kappa)E]\};\\ P_4=&(b'/\mu^2)(1-2\kappa-\mu\kappa)(AD-E^2)(BC-F^2)\\ =&(b'/\mu^2)[(1-\kappa)^2(1-\mu\kappa)\\ &-\kappa^2(1+2\mu-\mu\kappa)](AD-E^2)(BC-F^2).\end{aligned}$$

We may now try to correlate the very general, arbitrary constants A, B, C, D, E and F with certain force constants f_1, f_2, etc., which would be postulated on the basis of a simple physical model of the molecule. We would expect that for YX_3 the potential energy for small vibrations around an equilibrium configuration could be expanded in the form:

$$\begin{aligned}V=&V^0+(\partial V/\partial q)^0(\delta q_{12}+\delta q_{13}+\delta q_{23})\\ &+(\partial V/\partial r)^0(\delta r_1+\delta r_2+\delta r_3)\\ &+\tfrac{1}{2}(\partial^2V/\partial r^2)^0(\delta r_1^2+\delta r_2^2+\delta r_3^2)\\ &+\tfrac{1}{2}(\partial^2V/\partial q^2)^0(\delta q_{12}^2+\delta q_{13}^2+\delta q_{23}^2)+W, \quad (5)\end{aligned}$$

where W represents the potential energy due to the rigidity of the bonds, i.e., due to restoring forces perpendicular to the lines of bond.[7, 8, 9]

[5] J. B. Howard and E. Bright Wilson, Jr., J. Chem. Phys. **2**, 630 (1934), confirm this result previously given in reference 3 in 1932.

[6] The constant C used here is identical with C' of reference 4.

[7] Cf. the potential energy assumed for the pentatomic molecule by H. C. Urey and C. A. Bradley, Jr., Phys. Rev. **38**, 1969 (1931).

[8] A different expression for the potential energy of the pyramidal molecule based on chemical considerations has been given in reference 5.

[9] D. M. Dennison, Phil. Mag. **1**, 195 (1926), has considered the case: $W=0$.

These perpendicular forces are of two kinds: there are forces proportional to the change in angle between any two bond lines;[10] in addition there is a force proportional to the change in trihedral angle at the top of the pyramid. In the coplanar case the first force is in the plane of the X atoms, while the second one is perpendicular to it. Denoting the trihedral angle by $2S$ and the force constants (multiplied by suitable factors which simplify calculations) by f_4 and f_2, we obtain:

$$W=\tfrac{1}{2}\{[f_4(1+12g^2)(1+3g^2)]r^{02}(\delta\Omega_{12}{}^2+\delta\Omega_{13}{}^2+\delta\Omega_{23}{}^2)+[(1/9)(1+12g^2)^2f_2](r^0\delta S)^2\}. \quad (6)$$

It may be shown that in the case of the pentatomic molecule the two forces are identical.[11]

The condition of stable equilibrium for the non-vibrating molecule requires that $(\partial V/\partial q)^0=(\partial V/\partial r)^0=0$, whenever $g\neq 0$, and $(\partial V/\partial r)^0=-(\partial V/\partial q)^0\sqrt{3}$ for $g=0$. If we let:

$$(\partial^2 V/\partial r^2)^0=(1+3g^2)f_1;\quad (\partial^2 V/\partial q^2)^0=f_3;\quad (\partial V/\partial r)^0=q^0f_5/\sqrt{3}, \quad (7)$$

we obtain two different sets of relations connecting A, B, etc., with the various f's for the pyramid and the coplanar case. These relations are:

Pyramid		Coplanar Structure	
$A=3(f_1+\frac{2}{3}f_4)/2$		$A=3(f_1+\frac{2}{3}f_4+f_5)/2$	
$B=3(3g^2f_1+f_2+9g^2f_4)$		$B=3(f_2+f_5)$	
$C=\frac{1}{3}f_1+g^2f_2+f_3+9g^4f_4$		$C=\frac{1}{3}f_1+f_3$	
$D=\frac{1}{6}f_1+\frac{1}{3}f_3+\frac{1}{3}(1+6g^2)^2f_4$	(8)	$D=\frac{1}{6}f_1+\frac{1}{3}f_3+\frac{1}{3}f_4$	(8′)
$E=\frac{1}{3}f_1-\frac{2}{3}(1+6g^2)f_4$		$E=\frac{1}{3}f_1-\frac{2}{3}f_4-\frac{1}{3}f_5$	
$F=g(f_1-f_3-9g^2f_4)\sqrt{3}$		$F=0$	

(If we substitute in Eqs. (4) the constants A, B, C, etc., by their values as given by (8′) and let $f_2=f_4=0$, the resulting equations reduce to those given by Menzies,[12] supporting his formulae as against those given by Nielsen.[13])

Eqs. (8) contain implicitly the two relations of linear dependence between the constants A, B, C, D, E and F:

$$A(1+6g^2)+3E-B-(F\sqrt{3})/g=0,\quad 3(2D-C)+2E(1+6g^2)-F(1+3g^2)/g\sqrt{3}-\tfrac{1}{3}B=0. \quad (9)$$

They come in because the simplified model requires only four force constants for the pyramid, as compared with the six allowed by symmetry considerations. For the coplanar case, the potential energy must, for symmetry reasons, be an even function of z, so that $F=0$ independently of any special assumptions. Since in this case $f_5\neq 0$, the simplified model requires just as many constants as are allowed by symmetry considerations. Hence we can ascribe a definite physical meaning to *each* one of the general constants and determine unambiguously the values of the bond and other constants. The coplanar tetratomic and the collinear triatomic molecules seem to be the only ones of all the cases considered so far (triangular triatomic, pyramidal tetratomic, tetrahedral pentatomic configurations) where this is possible. For the other molecules, the determination of the physical force constants is dependent on the validity of expressions of the type of Eqs. (9). If experimental data (vibration frequencies, together with isotopic shifts) should show that the constants A, B, C, etc., are independent of each other, it would be necessary to postulate additional forces in order to account for the data. On the basis of a simple model, there is no obvious way of introducing these additional forces. Different assumptions could be made and corresponding to each one we would obtain a different value for the magnitude of the various forces. It is therefore questionable, whether any very definite meaning can be attached in general to terms like: "magnitude of the bond constant." But for the molecules YX_3, where the isotopic shifts are small, it is possible with four force constants to account for the data within the limits of uncertainty of the anharmonic corrections to the vibration frequencies.

In conclusion, I want to thank Professor H. C. Urey for his suggestions and interest in this problem.

[10] F. Lechner, Wien. Bericht **141**, 633 (1932), has considered the case where this particular force is the only one present in addition to the force along the bond.

[11] In the pentatomic case we have to take $\sum_{i=1}^{4}(r^0\delta S_i)^2$ for the four pyramids formed by the Y atom and any three X atoms. This sum is equal to a constant factor times $\sum_{i,j=1}^{4}(r^0\delta\Omega_{ij})^2$.

[12] A. C. Menzies, Proc. Roy. Soc. **A134**, 265 (1931).

[13] H. H. Nielsen, Phys. Rev. **32**, 773 (1928).

The Periodicity of Morse's Function

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The applicability of a simple modification of Morse's rule has been tested, and found generally satisfactory for simple non-hydride di-atoms and for hydrides of the *KH* period. Morse's function is shown to possess a periodic character, and to be capable of adjustment by the introduction of group numbers and period constants on the basis of the classification of di-atoms suggested by the present author. The contention that di-atoms should be regarded from the standpoint of their periodic group functions thus appears especially significant.

I. INTRODUCTORY NOTE

IN the present communication, the term "di-atom" is used in place of the conventional "diatomic molecule," for reasons which will be detailed elsewhere.

The author's proposed classification of di-atoms into periodic groups[1] has suggested a number of relations between their spectroscopic constants. In the course of this work, it was found possible to improve Morse's function (see Eq. (1) below) for simple non-hydride di-atoms.[2] The modification may also be applied to hydride di-atoms of the *KK* period and, with certain limitations, to more complex cases. The purpose of the present communication is to show the periodic character of the function.

The group number of a di-atom is defined by the total number of valency electrons of the constituent atoms, and denoted by n. It corresponds to the number of "shared" electrons, as distinguished from "non-bonding" electrons, the shared electrons having their atomic quantum designations more or less strongly modified when union occurs.

The classification of non-hydride di-atoms is essentially three-dimensional and consists of combining in all possible ways different pairs of non-bonding groups with different groups of shared electrons. The basis is a two-dimensional matrix of combinations between pairs of completed K, L, $M\cdots$ rings on a horizontal plane, as follows:

KK	*KL*	*KM*	....
LK	*LL*	*LM*	....
MK	*ML*	*MM*	....
.	.	.	
.	.	.	
.	.	.	
.	.	.	

Vertical lines, intersecting further horizontal planes defining molecular groups and sub-groups are then erected upon each compartment of the period matrix, used as a basal plane. The details will be communicated elsewhere.

The classification of hydride di-atoms is two-dimensional, periods being denoted by *K*H, *L*H, *M*H$\cdots$.

Elementary di-atoms are represented by symbols of the type *LiLi*, *NN*, *OO*, etc.

II. MORSE'S FUNCTION

Morse[3] proposed an empirical relation between the two fundamental magnitudes ω_e, the equilibrium nuclear vibration frequency for small amplitudes, and r_e, the equilibrium nuclear separation of a di-atom, to the effect that

$$\omega_e r_e^2 = \text{a constant}. \qquad (1)$$

Whilst several authors have pointed out that Morse's rule is subject in certain cases to considerable errors, no one appears to have investigated the matter systematically up to the present time.

A careful examination shows that the Morse expression, far from assuming a constant value, is a periodic group function of the atoms concerned, at any rate in the simplest cases where data are available.

[1] C. H. Douglas Clark, Proc. Leeds Phil. Soc. **2**, 502 (1934).

[2] C. H. Douglas Clark, Phil. Mag. [7] **18**, 459 (1934).

[3] P. M. Morse, Phys. Rev. [2] **34**, 57 (1929).

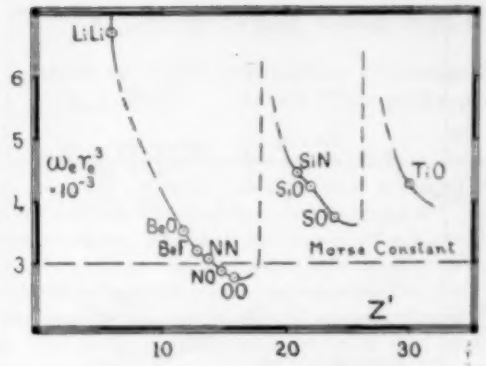

FIG. 1. The periodicity of Morse's function in the case of simple non-hydride di-atoms containing at least one completed K ring, in their ground states.

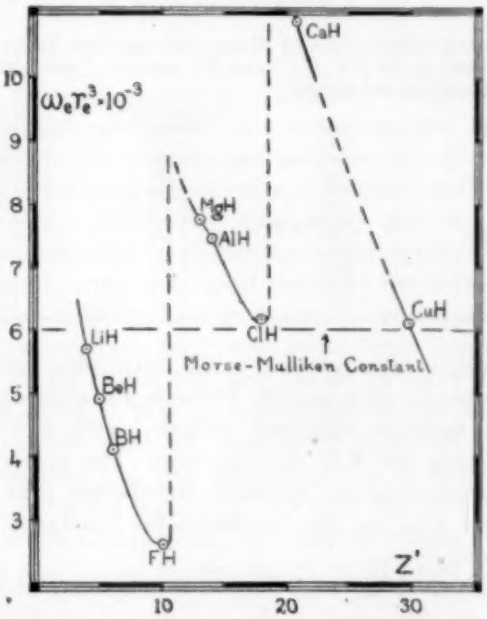

FIG. 2. The periodicity of Morse's function in the case of simple hydride di-atoms in their ground states.

The results are plotted in Fig. 1 (non-hydride di-atoms) and in Fig. 2 (hydride di-atoms) against the number of extranuclear electrons Z'. The periodic nature of the function is thus clearly demonstrated. The value of Morse's constant is taken as 3000 and 6000 for non-hydride and hydride di-atoms, respectively. The general form of the two curves is roughly the same. The apparent constancy of the function in the case of non-hydride di-atoms appears to have been due to the fact that the molecules considered were mainly those lying near the flattest portion of the first sweep of the curve in Fig. 1. Whatever correction is appropriate for modifying Morse's expression, it appears that this periodicity must be compensated for.

The author[2, 4] has suggested a simple modification of Morse's function to the effect that

$$\omega_e r_e^3 \cdot n^{1/3} = K \qquad (2)$$

where K is a constant throughout any simple period of non-hydride di-atoms or di-atom ions. With the introduction of appropriate period constants determined empirically and with the group number n as defined above in all cases, very considerable improvement in the accuracy of the relation has been obtained. This is shown in Table I, for non-hydride di-atoms.

TABLE I.

Period	Period constant K	Number of electronic states considered	r_e calculated from ω_e, Percentage average error: *Morse*	*Clark*
KK	9,550	29	5.2	1.3
KK^+	9,050	7	1.9	1.2
LK	12,850	7	9.2	1.3
	Mean errors		5.4	1.3

The importance of a relation of the Morse type lies in the fact that it enables r_e to be calculated from ω_e in undetermined cases. These constants are required in the construction of potential energy-nuclear distance curves, by means of formulae due to Kratzer, Morse and others. The constants in these formulae are directly related to the fundamental constants of the Morse function. These curves are likely to be found of increasing practical usefulness in the interpretation of the mechanism of chemical reaction.

III. Graphical Representation of the Proposed Modification of Morse's Rule, as Applied to Simple Non-Hydride Di-Atoms

Fig. 3 shows the mean percentage errors in r_e's for different cases in the KK, KK^+ and KL molecular periods, as calculated by the method of Morse (thick lines) and of the author (barred lines). It is observed that Morse's errors tend to

[4] C. H. Douglas Clark, Nature **133**, 873 (1934).

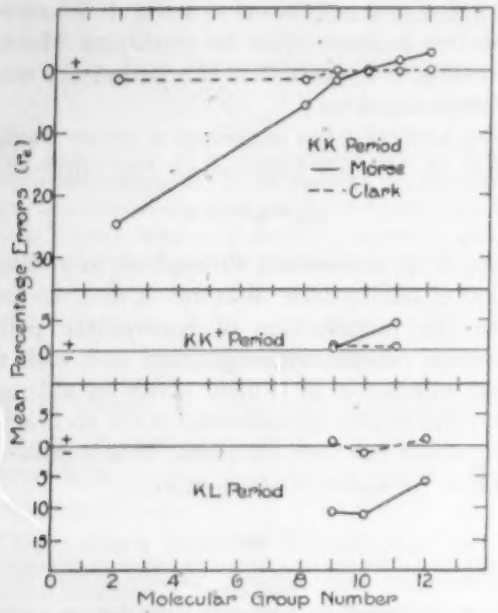

FIG. 3. Comparison of mean percentage errors in r_e by the Morse and the modified Morse expressions in the KK, KK^+ and KL periods of non-hydride di-atoms.

	Group	Morse	Clark
Period KK mean errors:			
	2	−24.7	−1.3
	8	−5.7	−1.9
	9	−1.9	0
	10	−0.2	0
	11	+1.4	−0.3
	12	+2.8	0
Period KK⁺:			
	9	+0.7	+0.9
	11	+4.8	+1.0
Period KL:			
	9	−10.5	+0.9
	10	−10.9	−1.3
	12	−5.8	+1.1

become increasingly positive with increasing group number in each period. In the KK period, Morse's errors become positive from a large negative error (*LiLi*). It thus happens that Morse's unmodified formula fits the facts best in the region of groups 9 to 11, where the line crosses the zero error line.

It should be borne in mind that in evaluating the cube of the equilibrium internuclear distance, any experimental error is correspondingly magnified. In comparing results obtained by the two methods, therefore, it is probably best to compare the function $r_e\omega_e^{1/3}$ with $r_e\omega_e^{1/3}n^{1/6}$. In Fig. 4, the logarithms of these functions to base 10 are plotted against molecular group numbers. The general parallelism of the two sets of curves amongst themselves is noteworthy. The Morse

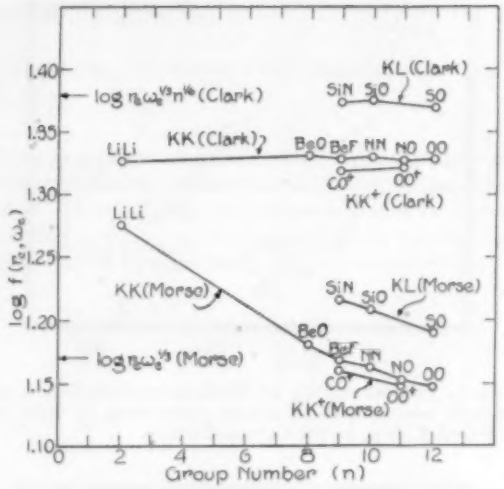

FIG. 4. Comparison of Morse and modified Morse expressions in the KK, KK^+ and KL periods of non-hydride di-atoms (ground states).

Period	*Mol*	log $r_e\omega_e^{1/3}n^{1/6}$ (*Clark*)	log $r_e\omega_e^{1/2}$ (*Morse*)
KK	LiLi	1.325	1.275
	BeO	1.331	1.181
	BeF	1.326	1.167
	NN	1.330	1.163
	NO	1.326	1.152
	OO	1.327	1.147
KK⁺	CO^+	1.319	1.160
	OO^+	1.322	1.148
KL	SiN	1.375	1.216
	SiO	1.375	1.209
	SO	1.370	1.190

functions *always fall* with increasing group number in each period. There is a *discontinuous* gap between different periods, with a small lowering for KK di-atom ions. The corrected expression gives *essential parallelism with the group axis*, as the condition for constancy requires.

Morse considered that with increasing atomic weight difference of the constituent atoms of a di-atom, an increasing correction of the type of an "asymmetry factor" $(4M_1M_2/(M_1+M_2)^2)^{1/4}$ might become necessary, where M_1, M_2 are the masses of the individual nuclei. When these masses are equal, the factor reduces to unity and therefore would not apply to the di-atom *LiLi*, where Morse's unmodified expression yields large errors in calculating internuclear distance of the order of 25 percent.[4] Hence it appears that, at any rate for the simpler cases, the correction should depend rather upon change of group number and of period, with a small correction for ionized states, as suggested by the present author.

Accommodation Coefficient of Mercury Ions on a Mercury Surface

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The pressure exerted on a mercury surface, to which were attracted mercury positive ions produced in a mercury arc, was measured by a modified form of Chattock micromanometer. The pressures found were entirely too large to be given by the neutralized ions alone, even if they had an accommodation coefficient of zero. The correction for the general heating of the mercury surface was not large. The most probable explanation is that each ion sputtered a large number of atoms and that the reaction on the surface of these escaping sputtered atoms gave the observed forces. If α is the accommodation coefficient, defined as the fraction of the energy of the impacting ions which is not carried away by the sputtered atoms; n, the number of atoms sputtered per ion; V_s, the electron volt equivalent energy of the sputtered atoms, then the experiments set these limits for 1000 volt ions:

$$100 > n > 7.8; \quad 0.92 > \alpha > 0; \quad 0.78 < V_s < 128.$$

The force exerted on the mercury surface was a linear function of the energy of the ions, represented approximately by

$$(F/i)(\text{dynes/amp.}) = 9V \text{ (volts)}.$$

From a critical examination of the sources of error, it seems the true forces must have been greater than the values used above.

AN accommodation coefficient for positive ions neutralized at a metal surface, analogous to the long known accommodation coefficient for neutral molecules, was first discovered by Van Voorhis and Compton;[1] defining the accommodation coefficient α as the ratio of the actual heating of a metal target to the expected heating if all the kinetic energy of the impacting ions were given up to the metal, they found α for A and Ne on Mo, and He on Pt to be 0.75, 0.65 and 0.35 to 0.55, respectively. Later measurements[2, 3] on the momentum imparted to a metal target by the neutralized ions gave for α, defined in the same way, but with energy translated into momentum, the average values 0.49, 0.84 and 1.0 for He on Mo, A on Mo and A on Al, respectively. Aside from its intrinsic interest, the accommodation coefficient of mercury ions on a mercury surface is of obvious importance in momentum and energy considerations at the cathode of a mercury arc.

EXPERIMENTS AND RESULTS

From the previous experiments and simple theory,[3] it was expected that the accommodation coefficient for mercury would be very close to 1; consequently, an extremely sensitive method of measuring the force on a mercury pool was sought. Of several possible ways, the simplest seemed to be the use of a Chattock micromanometer.[4] The usual design had to be altered considerably for the purpose of this experiment, and the water and castor oil commonly used were replaced by liquids of low vapor pressure and low viscosity. The final assembly is shown in Fig. 1, the micromanometer being mounted upon the tilting frame of the standard instrument made by the Cambridge Instrument Company.

Essentially the micromanometer consists of a U-tube employing two liquids of slightly different density. The surface of separation of the liquids occurs in a vertical limb, at the end of the narrow tube O. The interfacial tension of the liquids is large, and the levels are adjusted so that the heavier liquid forms a bubble in the lighter liquid at the end of O. The surface of separation is observed in a microscope M. As a third component, mercury, must necessarily be introduced, the decrease in sensitivity which results may be minimized by making the ratio of the areas of the mercury pools E and P to the area of O, as large as possible. The liquids chosen for the manometer were diethylene glycol, of density 1.1108 at 28.5°C, for the heavy liquid, and dibutyl phthalate, with a chlorinated diphenyl added to bring the density up to 1.0866, for the light.[5] By freezing the mercury in trap T, it was

[1] Van Voorhis and Compton, Phys. Rev. **37**, 1596 (1931).
[2] Lamar, Phys. Rev. **43**, 169 (1933).
[3] Compton and Lamar, Phys. Rev. **44**, 338 (1933).
[4] Chattock, Phil. Mag. **217**, 96 (1901); Stanton, Proc. I. C. E. **156**, 83 (1904); Chattock and Tyndall, Phil. Mag. **19**, 450 (1910).
[5] These were chosen because of their availability in the laboratory; the vapor pressure of the diphenyl compound was high enough, however, that a liquid air trap between

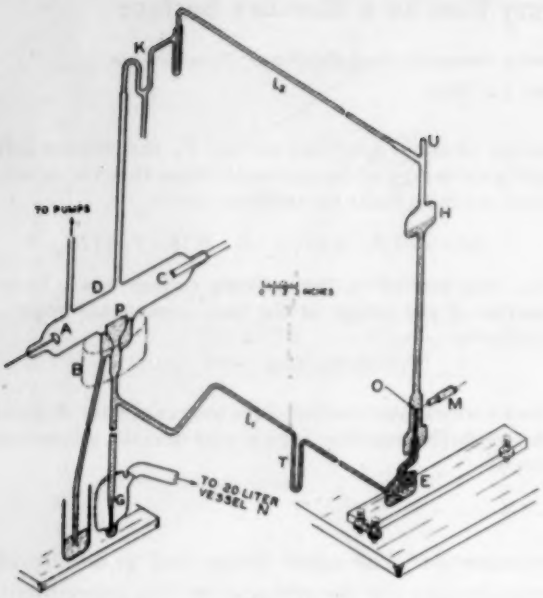

FIG. 1.

possible to introduce the manometer liquids at U in the proper sequence, with thorough pumping of the system at each step. The tubes L_1 and L_2 were sufficiently long and flexible to permit considerable adjustment of the levels of the liquids, and in particular, the surface of separation at O could be brought to the desired position, by moving the micromanometer relative to the tube D and pool P.

Because of rapid changes in atmospheric pressure produced by convection currents in the room, it was necessary to close the vessel G by connection to a 20 liter container. Changes in the temperature of N also produced pressure changes, but these were slow and could be compensated for by the adjustment of the micromanometer.

The device was calibrated by raising the cut-off K so that the pressure on H remained constant, and then changing the gas pressure in D. The change in pressure on P, read directly on a McLeod gauge, produced a change in the position of the surface of separation at O which was observed in a micrometer eyepiece in M. The sensitivity of the device was such that steady pressure differences could be read to 0.1 dyne per sq. cm, and rapidly changing pressure differences, to 0.5 dynes per sq. cm.

Positive ions were produced by an arc between the thermionic cathode C and anode A. The electron temperature, electron density and space potential were determined by using P as a Langmuir probe. In all tests the residual gas pressure was less than 10^{-4} mm, so substantially only mercury ions were present. It was not possible to bake out the tube or distill in the mercury, but the mercury was double distilled before being put in G and the containing tubes were carefully washed out. The surface at P was frequently changed by overflowing.

In order to measure the reaction on P when it collected positive ions, the bubble at O was adjusted to a desired position on the M eyepiece scale with P insulated; then suddenly, a large negative voltage was applied from P to A. Any change in the pressure on P, due to the impact of the positive ions, resulted in a movement of the surface of separation at O, because the pressure on H was unaffected by application of voltage to P. Ideally, the manometer is supposed to be tilted so as to keep always the same position for the surface of separation at O, but practically it was found the magnitude and rapidity of the changes were too great for this. As the best alternative, the deflection of the interface for different pressure changes was determined by direct calibration. Thus, for any change in position on the eyepiece scale, the change in the force acting on P was known. That this method was sufficiently accurate was checked by its reproducibility. The manometer was always calibrated immediately after a series of tests, and the calibration changed but little from day to day.

At first, it was almost impossible to keep the bubble at the zero position of the scale, because of the effect of temperature changes in the tube D, and particularly because of the thermal expansion of the mercury in P and its connecting tube of different diameter. By raising the level of mercury in the overflow tube surrounding P almost to the same level as the mercury in P, and by placing a cooling bath B around both, the drifting of the manometer with P insulated was almost eliminated. The most consistent results were obtained with a melting ice bath in B.

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the manometer and discharge tube was necessary. A better choice for the light liquid would seem to be benzyl butyl phthalate or methyl butyl phthalate, as suggested to me by the Commercial Solvents Corp.

As the force acting on P proved to be a function of time, the usual procedure was to bring the surface of separation at O nearly to the desired zero position by means of the leveling screws on the micromanometer frame. Then, the position of the interface in the eyepiece scale was read every few seconds, the time being noted on stop watches. After several seconds with P insulated—long enough for the steady drift to be secured—negative voltage was applied to P, and readings continued for perhaps 1 or 2 minutes. Usually, voltage was then removed, and readings obtained for several seconds longer.

In addition to the reaction of the neutralized ions leaving the mercury surface, a force may be imparted to P as a result of the heating of the surface by positive ion impact. The magnitude of the heating effect alone may be found by heating the surface by other means—by electron bombardment, for instance. If P is made slightly negative with respect to space, the electrons reaching it move under a retarding field, so the average energy of the electrons striking the surface is $2kT_e$ where T_e is their temperature in the discharge. The watts input per ampere of electrons is $2kT_e/e+\varphi_-$ where φ_- is the heat of condensation of the electrons, arbitrarily taken at 4 volts. The mass of the electrons is so small, the momentum involved is negligible. The number of positives striking the surface is practically the same as when a large negative voltage is used, but their energy is so much less (pool 1.5 to 4 volts negative to space as compared to 50 to 1000 volts) that their effect is also negligible.

The effect of heating the mercury is twofold; first, the increase in temperature causes a relatively large increase in the number of atoms leaving the surface, and possibly an increase in the number striking the surface. Consequently, the pressure on the surface is increased. Second, if the surface and vapor were in equilibrium before the heating started, then the number of atoms leaving the surface, after the temperature increases, is greater than the number striking, so a net loss of mass results. This is interpreted by the micromanometer as a *decrease* in pressure on the pool P. If the mean free path were large compared to the dimensions of the tube D, then one could write for the change in force on P when it is heated,

$$\Delta F=(p-p_0)/2-a\int_0^t(p-p_0)dt, \qquad (1)$$

where p_0 represents the pressure of Hg vapor in the tube at $t=0$, when the heating starts; p, the pressure of Hg vapor corresponding to the temperature of the surface at a time t; and a, a constant given by kinetic theory as 0.034. The temperature of the surface, and consequently p, is an increasing function of the time of heating; it eventually reaches a constant value, however, when all the heat input is lost by conduction or evaporation. Now actually, the vapor density is such that the m.f.p. is short compared to the dimensions of D, so the actual ΔF cannot be represented by an equation as simple as (1): the first term should be greater than given in (1), and the second term should be less, with a no longer constant but a function of both p and p_0. Eq. (1) does give an indication, however, of what may be expected; the force ΔF is zero for $t=0$, increases to a maximum, and then continually decreases because of the last term. A typical illustration may be found in Fig. 2, where the deflection of the manometer for electron heating of P is plotted against time; the point "on" shows when the electron current to P was initiated.

When positive ions strike the test pool, the force is

$$\Delta F=W(T)+I-St, \qquad (2)$$

where $W(T)$ represents the effect of general heating, I is the reaction resulting from an accommodation coefficient less than 1, and S gives the rate of sputtering, to be discussed in the next section. If equilibrium is established before the application of negative voltage to P, then $W=0$ when $t=0$, so the initial value of ΔF

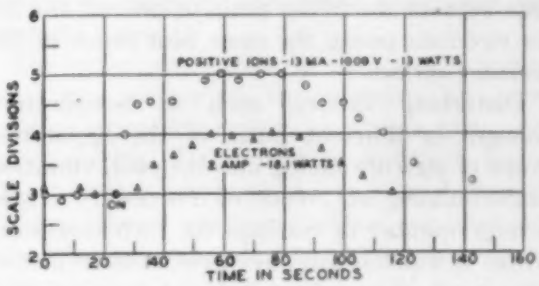

FIG. 2.

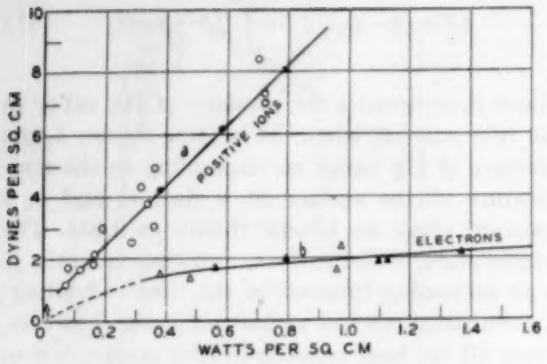

FIG. 3.

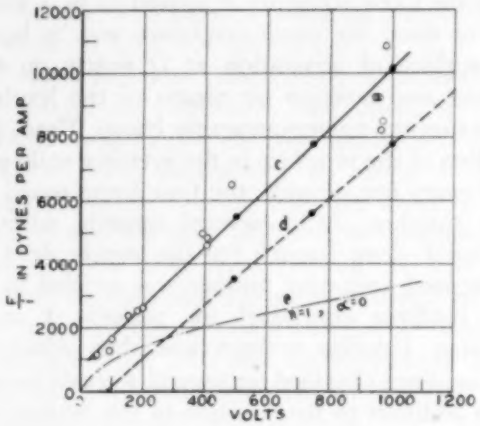

FIG. 4.

is simply I. Thus if one could measure ΔF for very short times, then I could be found at once. Unfortunately, the micromanometer has considerable time lag, chiefly due to the inertia of the large masses of mercury in pools E and P: with a suddenly applied force about 8 seconds elapses before the deflection of the manometer reaches 90 percent of its final value. Instead of the positive ion response being a sudden increase, followed by a slow rise to maximum, the time lag of the instrument causes it to show a fairly rapid rise, followed by slower increase to maximum, as shown in Fig. 2. It is impossible to extrapolate such a curve to $t=0$ with accuracy. Consequently, the following procedure was adopted: for positive ion bombardment the value of ΔF at the end of the rapid rise (from 6 to 10 seconds after voltage was applied) was read; this is somewhat less than the true value of ΔF for $t=10$ sec., because of the lag of the instrument and because the readings were often for times a little under 10 sec. For electron heating, the value of $\Delta F = W(T)$ at 10 seconds was determined. Now the true value of I, the reaction due to the impacting ions is greater than the difference between the ΔF for positive ions and the ΔF for electrons giving the same heat input to the mercury surface.

Disturbing factors, such as temperature changes in different parts of the apparatus, drops of mercury falling into the pool, vibration of the building, etc., rendered it necessary to take a large number of readings for each condition. Those in which it was obvious extraneous factors were involved were discarded, and the remainder, usually from 4 to 10, were averaged to get the data which are plotted in the accompanying figures. Fig. 3 shows the increment in pressure on the pool P plotted against watts per sq. cm input to the pool, both for electron and positive ion impacts. In Fig. 4, the force observed divided by the positive ion current is plotted against the potential of the pool negative to space, for curve c; for curve d, the observed force for positive ions is first decreased by the ordinate of curve b, Fig. 3, for the corresponding watts input. Curve d, presumably gives the force per ampere of positive ions, resulting from an accommodation coefficient less than 1. The most reliable data are indicated by the solid points.

For voltages less than about 50, the forces for the largest obtainable positive ion currents were too small to be read with accuracy; for voltages greater than 1000 and currents above 1 m.a. per sq. cm the forces were too large to be read by the micromanometer in its present form. Typical data for one particular test are recorded below; the ranges covered in all the experiments are listed in the parentheses.

Test 9–24; arc 10.4 amp. (1.5–20), 26 volts (18–26); electron temp. 29,300°K (9600–30,200); random electron current, over 280 m.a./cm² (33–280); random pos. ion current, 0.805 m.a./cm² (0.09–1.73); space pot. 5.5 volts negative to A (5.5–10.5); dark space thickness, 0.51 cm; temp. cooling bath 4° (2° to 5° when cooled); applied voltage P to A 1000 (60–1000); pos. ion current, 13.1 m.a. (2.74–28.4); initial deflection 1.55 div. = 8.04 dynes/cm² (1.78–8.4); area of P, 16.45 cm².

Discussion of Results

The momentum delivered to the mercury surface by the impacting positive ion is just balanced by the electrical forces exerted on the mercury; however, if the neutralized ion leaves the surface with some of the kinetic energy it acquired in falling through the space charge sheath, then the momentum imparted to the surface is

$$mv = m(1-\alpha)^{\frac{1}{2}}(2eV/m)^{\frac{1}{2}},$$

where α is the accommodation coefficient and V is the potential drop in the space charge sheath. If the neutralized ions leave in random directions, then the average normal component of momentum is only $\frac{1}{2}$ the above. If a current i of mercury positive ions flows, then the pressure on the mercury pool should be

$$F_{\text{dynes/cm}^2} = 100\, i_{\text{amp./cm}^2} V^{\frac{1}{2}}_{\text{volts}}(1-\alpha)^{\frac{1}{2}}. \quad (3)$$

For α independent of V as previous experimenters have found approximately true, then F/i should be proportional to $V^{\frac{1}{2}}$. The maximum possible value of F/i is given by putting $\alpha=0$ (i.e., assuming the ions are elastically reflected upon neutralization); such a maximum is plotted in curve *e*, Fig. 4. One sees that *e* lies below all of the uncorrected experimental points; and if $\alpha=0$, then no energy is given to the mercury surface, and no correction for heating of the surface should be applied to the measured forces. Only possibly for positive ion energies less than 100 volts can the experimental points agree with Eq. (3); and for energies of 1000 volts, the discrepancy is wide. Furthermore, the experimental data show F/i is proportional to V and not to $V^{\frac{1}{2}}$ as Eq. (3) would require. Thus both in magnitude and way of variation with energy of the positive ions, the observed forces cannot be exerted by the neutralized ions alone.

For a given total energy, the momentum is proportional to the square root of the mass involved; so, one can account for the observed forces by supposing many atoms react upon the mercury surface for every ion measured. This can occur if an ion makes several collisions in passing through space charge sheath. With momentum conserved, the total momentum given to the mercury surface by all the impacting particles, both the ion and the neutral atoms with which it has collided, is still balanced by the electrical force on the mercury. If, however, the neutral atoms also have an accommodation coefficient less than one, then the reaction of these atoms and the neutralized ion leaving the mercury yields a net force on the mercury. The question thus arises, is the mean free path of the mercury ion less than the space charge sheath thickness?

The mercury vapor density in the discharge tube is not known precisely, but it may be estimated as follows: in order to carry away the heat input to the mercury, in the steady state with the pool insulated, a temperature drop of less than 20° between the surface of the pool and the outside of the discharge tube, is estimated from the dimensions and geometry of the mercury pool P and the mercury surrounding it in the overflow reservoir. The temperature of the outside tube wall was perhaps 50° in the early tests, but when a cooling bath was used, as was the case for all the data plotted in Figs. 3 and 4, the temperature of the bath was between 2° and 15°; when the best data were obtained, the temperature was 2° to 4°. The temperature of the mercury surface, then lay between 20° and say 40°; the corresponding vapor pressures are 0.0012 and 0.0061 mm. At these pressures, the mean free path of the mercury *atom* would be 1.37 and 0.27 cm. For many of the trials, the m.f.p. of the mercury ion was certainly greater than 1 cm. The space charge sheath thickness was observed visually in a number of cases, and could be calculated of course; the measured values were about 30 percent higher than the calculated (see below). The greatest thickness, for 1000 volt applied to the probe, was only 0.76 cm. Though some collisions undoubtedly occurred within the sheath, it seems very unlikely that a sufficient number of collisions were made to account for the large forces.

The other alternative is that many atoms leave the surface of the mercury for each positive ion which strikes, or as one may say, the *sputtering* of the mercury surface is large. This is reasonable from the v. Hippel theory[6] which attributes sputtering to local vaporization from a limited area, raised to a high temperature

[6] v. Hippel, Ann. d. Physik **81**, 1043 (1926); Blechschmidt and v. Hippel, Ann. d. Physik **86**, 1096 (1928).

for a very short time by the impact of a positive ion. The time the temperature remains high enough for rapid vaporization is inversely proportional to the thermal conductivity of the material. The rate of vaporization depends upon the vapor pressure of the material, which can be approximated by $p=Ae^{-\lambda/kT}$, where λ is the heat of vaporization per molecule. Sputtering thus is influenced to some extent by the thermal conductivity, but to a much greater degree by the latent heat of vaporization, since the latter occurs in the exponential. The v. Hippel theory does not attempt a quantitative explanation of sputtering, but it is successful in predicting the relative order in which the metals sputter. Data for the sputtering of mercury are not available, but the sputtering of other metals by 1000 volt mercury ions is between 1 and 5 atoms per ion.[7, 8, 9] Consider the value for platinum, 1.75 atoms per ion:[8] the thermal conductivity of platinum is about 8 times that of mercury, while the latent heat of vaporization of platinum is almost 10 times that of mercury; the sputtering rate of mercury must be far greater than that of platinum. The thermal conductivity, and particularly, the heat of vaporization are so much less for mercury than for the metals for which little sputtering is found, that it would not be surprising to find the sputtering of mercury to be greater by one or two orders of magnitude.

A distinction should be made between the local vaporization or sputtering and the general vaporization, which occurs uniformly over the surface. Any reaction due to the latter is included in the correction made for the effect of heating the mercury surface; the former is directly attributable to the positive ion impacts.

If many atoms leave the mercury surface near the point of impact of a positive ion, it is useless to inquire which is the neutralized ion and with what velocity it leaves; experiment gives only the reaction of all the atoms. The definition of accommodation coefficient may be generalized, to cover the present case, with the following simplifying assumptions: suppose the sputtered atoms, including possibly but not necessarily the neutralized ion as one of their number, all have the same velocities which are distributed randomly in direction away from the surface; let $n=$No. of sputtered atoms per incident ion, $v=$velocity of emission, $m=$mass of individual atom. Define α, the accommodation coefficient, as

$$\alpha=(eV-\tfrac{1}{2}mnv^2)/eV. \tag{4}$$

The pressure exerted on the surface will be

$$F=i/e\cdot\tfrac{1}{2}mnv. \tag{5}$$

Now, from Fig. 4, the force on the mercury surface is seen to be almost directly proportional to the energy of the impacting ion, with a small uncertainty involving the correction for general heating. Approximately, then

$$F/i_{\text{dynes/amp.}}=9V, \tag{6}$$

where V is the energy of the ion in electron volts. Substituting in the expression for α, and changing to practical units

$$\alpha=1-7.8\times10^{-3}V/n. \tag{7}$$

The kinetic energy of an individual sputtered atom,

$$\tfrac{1}{2}mv^2=eV_s \quad \text{say, is} \quad V_s=7.8\times10^{-3}(V/n)^2. \tag{8}$$

Now α defined in this way must be positive, so

$$n\geqslant 7.8\times10^{-3}V. \tag{9}$$

An idea of the upper limit of n may be obtained from the rate of change of ΔF with t; in Eq. (2), if none of the sputtered atoms return to the mercury pool $S=n(i/e)mg$. Since W is also a function of t, through the temperature, S cannot be greater than $-d\Delta F/dt$. For $V=1000$, the experimental data show that n must be less than 100. So these rough limits may be fixed, for $V=1000$

$$100>n>7.8, \qquad 0.92>\alpha>0, \qquad 0.78<V_s<128.$$

It seems likely the true values are nearer the left-hand limit than the right.

Sources of Error

The micromanometer could be read with an error of not over 0.5 dyne per sq. cm; the percentage error thus was large at very low voltages

[7] Meyer and Guntherschulze, Zeits. f. Physik **71**, 279 (1931).
[8] Henderson and Gideon, Phys. Rev. **43**, 601 (1933).
[9] Compton and Langmuir, Rev. Mod. Phys. **2**, 188 (1930).

but became about 5 percent at the highest voltages.

The energy the positive ions acquired in the accelerating field at the mercury surface was known to within 2 volts. Some doubt exists, however, as to the number of positive ions. The measured current included both the positive ions and any secondary electron emission from the mercury surface. For 1000 volts applied to the probe, the space charge sheath thickness calculated from the Langmuir space charge equation upon the basis of no collisions by the positive ions was less than the measured value by almost 30 percent. The tube was so constructed that the sheath thickness could not be measured accurately but it seems the error in measurement must have been less than 30 percent. Edge effects would make the average current density, used in calculating the sheath thickness, greater than the actual current density at the center of the pool, where the thickness was measured; thus the calculated thickness would be too low. The effect of collisions of positive ions within the sheath would tend to make the actual thickness less than the calculated,[1] rather than greater. The secondary electron emission would have to be almost 80 percent of the positive ion current, in order to bring up the calculated thickness to the measured. This is larger than the secondary emission found for Hg ions on Ni, W and Pt by other investigators,[8–12] who report values from less than 10 to 40 percent. From the work of Sonkin[13] it seems unlikely that any large emission by metastable atoms occurred. Possibly some photoelectric emission occurred. The force per ampere calculated above, being based on the measured current, is less than the actual force per ampere of positive ions, if electrons were emitted from the mercury surface.

The heating effect of electrons is uncertain to the degree that the heat of condensation differs from the assumed value of 4 volts. In calculating the heating by positive ions, merely the product of measured current and voltage to space was used; the unknown heat of condensation of the positive ions was neglected. More important considerations, and effective in the opposite direction, are the heat carried away by the sputtered atoms and the inclusion of any secondary electrons as heating current. The actual heating must be considerably less than the measured iV used, so the correction subtracted from the observed positive ion forces is too large.

Some of the pressure attributed to the effect of heating when electrons are attracted to the pool might conceivably be due to sputtering by the electrons. The energy contributed by an electron is more likely to be generally distributed, so no local high temperature occurs, than the energy would be for a positive ion. Furthermore, the kinetic energy of the electrons was less than 5.2 equivalent volts. Experiments of Bariess[14] showed no electron sputtering for 800 volt electrons; though his data are incomplete, from approximate calculations it seems that the sputtering in his case must have been less than 10^{-3} atom per 800 volt electron. Other experiments[15] record a disintegration of a sputtered deposit by electrons only for energies greater than 2000 volts. General heating of the mercury seems to be the only possible effect when electrons strike the surface.

Calculations show that any direct change in surface tension through the presence of an electric field or the change in temperature of the mercury surface caused an entirely negligible deflection of the micromanometer. The effect of a change in the angle of contact between the mercury pool and the glass tube P, due to the above factors, is not so easy to estimate, but it also appears to have been inconsiderable.

Changing the arc current by 2 amp., or applying a large negative voltage to the mercury in the overflow reservoir surrounding P, caused no deflection when the test pool was insulated; thus any effect of change in current distribution in the tube when electrons or positive ions were collected by P must have been negligible.

The electron pressure to which Tonks[16] has called attention, is negligible; when the mercury surface was changed from insulated to 1000 volts negative, the electrons reflected from the surface,

[10] See Rev. Mod. Phys. **2**, 177 (1930).
[11] Oliphant, Proc. Roy. Soc. **A132**, 631 (1931).
[12] Chaudhri, Proc. Camb. Phil. Soc. **28**, 349 (1932).
[13] Sonkin, Phys. Rev. **43**, 788 (1933).
[14] Bariess, Zeits. f. Physik **68**, 585 (1931).
[15] Johnson and Harris, Phys. Rev. **45**, 630 (1934).
[16] Tonks, Phys. Rev. **46**, 278 (1934).

and the electron pressure, changed by about 1 part in 400; when the mercury was changed from insulated to a few volts negative to space, so a large electron current was collected, the electron pressure decreased by less than a factor of 2. Since the total electron pressure, which was calculated from the measured temperature and density of electrons, was just below the limit of sensitivity of the micromanometer, consequently its effect could never be detected.

When the pool was insulated, it was actually about 5 to 15 volts negative with respect to space; thus, when a larger negative voltage was applied, the positive ion current remaining about constant, the *change* in pressure, which was the quantity measured, was smaller than the actual pressure which would be produced by ions of the applied voltage. The difference became considerable only for low negative voltages; as for these voltages, the uncertainties in the measurements were so large, a correction cannot be obtained.

Finally, if the sputtered atoms, before reaching the tube walls or before being scattered, communicated their momentum to other mercury atoms directly above the mercury pool, then the pressure of mercury vapor on the pool was reduced. Thus, the measured change in force actually was less than that corresponding to the reaction of the sputtered atoms.

Of all the factors mentioned above, a preponderance indicates the actual force on the mercury surface was greater than that given by curve *d* in Fig. 4. The approximate linearity of the relation between F/i and V shows that if the number of sputtered atoms is proportional to the energy of the positive ions, as many experiments indicate, the energy of the sputtered atoms must be constant. The data are not accurate enough to decide whether a minimum voltage exists below which sputtering does not occur. From Fig. 4, such a minimum must be less than 75 volts, as curve *d* is certainly too low. Consequently, direct application of these results to the cathode of an arc is not possible. As sputtering of tungsten has been found for 25 volt A ions,[17] it seems quite possible that mercury ions cause sputtering of the mercury cathode of a mercury arc with a 10 volt cathode fall. If the data reported herein can be extrapolated so far, then it appears an accommodation coefficient certainly less than 0.9 must be used in energy and momentum balance calculations for the mercury arc.

The writer is indebted to his associates in the Westinghouse Research Laboratories for advice about the choice of materials and the performance of the experiments.

[17] Holst, Physica **4**, 68 (1924).

LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twentieth of the preceding month; for the second issue, the fifth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

On the Nuclear Radius

According to Eastman's[1] interpretation of Heisenberg's equation, we have $r' = r_0 M^{\frac{1}{3}}$, where r' is the nuclear radius, r_0 a proportionality constant, and M the isotopic weight. In this connection, it was considered interesting to plot in Fig. 1 the nuclear radius r' against $A^{\frac{1}{3}}$, where A is the chemical atomic weight of the product nucleus, chosen because it gives a convenient average of isotopic weights and relative abundance of isotopes. The nuclear radii for elements of light weight were calculated from Pollard's[2] barrier heights according to $r' = 2Z^*e^2/U$, where U is the barrier height, and Z^* the atomic number less two. These values are in good agreement with those suggested by Riezler.[3] The barrier heights observed by Duncanson and Miller[4] and those to be had from Klarmann's[5] results were not included in Fig. 1, since it was felt that with other workers, disagreeing as to the shape of the potential barrier curve, the results would not be consistent with those obtained by Pollard. In fact, in calculating U for C and Al, Pollard used a somewhat different method, and it is seen that r' for these elements falls somewhat off the curve. The radii for the heavier radioactive elements were computed from Gamow's equation[6]

$$\lambda = (h/4mr'^2)\exp(-4\pi[2m]^{\frac{1}{2}}/h)\int_{r'}^{r^*}(2Z^*e^2/r - E)^{\frac{1}{2}}dr,$$

where $r^* = 2Z^*e^2/E$, λ is the decay constant, m the mass of the alpha-particle, E the energy of the alpha-particle. The radius, r', is here defined as the lower limit of the integral. For the purposes of this calculation the integral was graphically evaluated thus avoiding the errors found in the approximation. From Fig. 1, it will be noted that r' is linearly dependent on $A^{\frac{1}{3}}$, and not proportional as given by the theory above, not only for the light, but also for the heavy nuclei. Also, although the slope of the lines for the light and heavy elements may be taken as parallel, they do not form a continuous curve. When r' is plotted against the first power of A, a smooth curve, not a straight line, is obtained for the light elements. When r' is plotted against the atomic number, a random distribution of radioactive nuclei is obtained, which must be analyzed into distinct family components for a semblance of order. Thus it is seen empirically that the best results are obtained by plotting r' against $A^{\frac{1}{3}}$. Analysis of the figures in Table I leads one to note that roughly, with the exception of RaAc, those elements furthest off the curve give off complex radiation. In these cases of complex radiation, only the strongest group was used in the calculations. The elements, Pa, Ac C′, Th, and Th C′ were omitted because of discrepancies in the observed values of the decay constant.

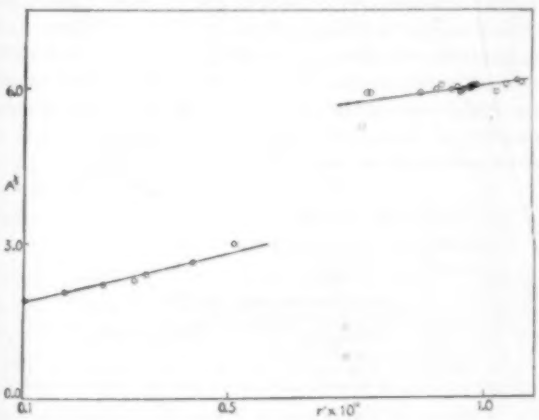

FIG. 1.

TABLE I.[7]

Parent nucleus	r'	Parent nucleus	r'
Li	0.10×10^{-13}	Ra C	1.03×10^{-13}
Be	.18	Ra C′	0.95
B	.26	Ra F	.88
C	.32	Ra Ac	.92
N	.34	Ac X	.95
F	.43	An	.91
Al	.51	Ac A	.94
U_1	1.07	Ac C	.78
U_2	1.08	Ra Th	.99
Io	1.05	Th X	.97
Ra	.98	Tn	.97
Rn	.98	Th A	.95
Ra A	.96	Th C	.77

ARTHUR K. SOLOMON

Harvard University,
Cambridge, Massachusetts,
November 20, 1934.

[1] Eastman, Phys. Rev. **46**, 1, 744 (1934).
[2] Pollard, Phil. Mag. **16**, 1131 (1933).
[3] Riezler, Proc. Roy. Soc. **A134**, 154 (1931).
[4] Duncanson and Miller, Proc. Roy. Soc. **A146**, 417 (1934).
[5] Klarmann, Zeits. f. Physik **87**, 411 (1934).
[6] Gamow, *Constitution of Atomic Nuclei and Radioactivity*, p. 49 (Oxford, 1931).
[7] Data secured from: *International Radium Standards Commission*, J. Am. Chem. Soc. **53**, 2437 (1931); Rutherford, Chadwick and Ellis, *Radiations from Radioactive Substances* (Cambridge, 1930); Gamow, *Constitution of Atomic Nuclei and Radioactivity* (Oxford, 1931); Kovarik and Adams, Phys. Rev. **40**, 718 (1932); Gratias, Phil. Mag. **17**, 491 (1934); Walling, Zeits. f. physik. Chemie **10** (6), 467B (1930); Collie, Proc. Roy. Soc. **A131**, 541 (1931); Soddy, Phil. Mag. **12**, 939 (1931); Gleditsch and Foyn, Am. J. Sci. **24**, 387 (1932); Jacobsen, Nature **133**, 565 (1934); Fesefeldt, Zeits. f. Physik **86**, 9–10, 605 (1933); Barton, Phil. Mag. **2**, 1273 (1926); Briggs, Proc. Roy. Soc. **A118**, 549 (1928), **A139**, 638 (1933), **A143**, 604 (1934); Geiger, Zeits. f. Physik **8**, 45 (1921); Laurence, Trans. Nova Scotia Ins. Sci. **17**, I, 103 (1927); Rosenblum, Comptes rendus **190**, 1124 (1930), **193**, 848 (1931), **194**, 1154 (1932), **195**, 317 (1932); Laurence, Proc. Roy. Soc. **A122**, 543 (1929); Rosenblum and Dupouy, Comptes rendus, **194**, 1919 (1932); Rosenblum and Chamié, Comptes rendus, **196**, 1663 (1933); Rutherford, Wynn-Williams and Lewis, Proc. Roy. Soc. **A133**, 351 (1931); Rutherford, Ward and Lewis, Proc. Roy. Soc. **A131**, 684 (1931); Rutherford, Wynn-Williams and Bowden, Proc. Roy. Soc. **A139**, 617 (1933).

The Origin of the Hardening of Cosmic Rays in Passing Through Matter

Let N_θ be the rate of production of cosmic-ray showers of any given type per cc per unit solid angle at some assigned angle θ to the vertical. In a recent communication,[1] the writer has developed the consequences of the assumption that N_θ increases with the energy E of the primary rays more rapidly than would be represented by a linear law. For purposes of mathematical illustration the form

$$N_\theta = \alpha_1 E + \alpha_2 E^2 + \cdots \text{etc.} \tag{1}$$

was assumed. It was supposed that the α's were functions of the atomic number of the medium and that for air, only α_1 was of importance. The fact that dE/dx is proportional to N_θ leads to an exponential law for the decrease of energy in passing through the atmosphere, and so to an exponential law for the corresponding intensity of shower production. Moreover, the assumption that for high atomic numbers the terms of importance in (1) involve higher powers of E than the first lead to the conclusion that the rate of shower production in lead, for example, should increase with altitude more rapidly than the measured cosmic-ray intensity, a fact in harmony with the observations of T. H. Johnson,[2] B. Rossi and S. de Benedetti[3] and J. C. Street[4] on small showers, and with those of C. G. and D. D. Montgomery,[5] and of R. D. Bennett, G. S. Brown and H. A. Rahmel[6] on showers of larger sizes, or Hoffmann Stösse as they are called.

All of this is for the case where the primary cosmic rays are of a uniform energy before entering the atmosphere, and where the measured cosmic-ray intensity is that produced by the showers initiated by the primaries whose directions of motion these showers perpetuate. It is the object of the present note to show that if we generalize the foregoing ideas to the case where even for air, the nonlinear terms in (1) play a part, we obtain a type of variation of measured cosmic-ray intensity with altitude which departs from the first approximation of an exponential form in a manner in harmony with experiment.

Thus, if in general we write, for air,

$$N_\theta = f(E) \tag{2}$$

and if, in line with the assumptions of the former paper we assume that the energy is lost entirely by shower production, we have

$$dE/dx = -\beta N_\theta = -\beta f(E), \tag{3}$$

where dx is an element of length of path of the primaries.

Hence, $$-(1/N_\theta)(dN_\theta/dx) = -(dE^2/dx^2)/(dE/dx).$$

Since
$$d^2E/dx^2 = -\beta f'(E)dE/dx,$$
$$-(1/N_\theta)(dN_\theta/dx) = \beta f'(E). \tag{4}$$

Now the left-hand side of (4) is the *apparent* coefficient of absorption μ which would be measured by an observer for any point if the observer assumed an exponential form $N_\theta = N_{\theta_0} e^{-\mu x}$, and obtained μ by measuring the infinitesimal percentage change in N_θ for a corresponding infinitesimal change in dx. We see that this apparent μ increases with E if $f(E)$ increases more rapidly with E than would be given by a linear law; for, in that case, $f'(E)$ will increase with E.

Hence, we see that the assumption of a *single* energy for the rays entering the atmosphere leads, on the foregoing views, to a decrease of intensity with depth below the top of the homogeneous atmosphere of such a nature that the apparent absorption coefficient μ decreases as we approach the earth, since E decreases with depth below the top of the atmosphere. This conclusion is in harmony with the apparent hardening of the rays as they pass through the atmosphere.

In the case where the medium is of high atomic number, and where, consequently, the nonlinear terms of (1) are more important than for air, the hardening should be more pronounced than for air. Thus, writing (4) in the form $\mu = \beta f'(E)$ and using (2), we have

$$(1/\mu)(d\mu/dN_\theta) = f''(E)/[f'(E)]^2.$$

Taking a case where $f(E) = \alpha_n E^n$,

$$(1/\mu)(d\mu/dN_\theta) = \alpha_n n(n-1)E^{n-2}\alpha_n^{-2}n^{-2}E^{2n-2}$$
$$= [n(n-1)/n^2]/\alpha_n E^n = n(n-1)/n^2 N_\theta.$$

Thus if $\delta\epsilon_\mu$ is the percentage change in μ corresponding to the percentage change $\delta\epsilon_N$ in N_θ

$$\delta\epsilon_\mu/\delta\epsilon_N = n(n-1)/n^2.$$

Thus, if we measure the intensity of the showers emerging from a cylinder of lead for different thicknesses of the lead, the percentage change in μ per unit change of shower intensity caused by change in thickness should increase with n from the value zero for n = unity to a maximum determined by n = infinity. In other words, the *hardening* of the rays as understood in the more exact sense exemplified above, should be greater in the case of lead than in that of an element of lower atomic number.

The whole of the foregoing discussion has been made in terms of a radiation having a definite and unique energy before entering the atmosphere; and its purpose is to show the extent to which the phenomena considered may be accounted for on the basis of such a simple hypothesis. The consequences here developed are, however, applicable in the case of a nonhomogeneous primary radiation, and the most natural conclusion would be to suppose that such nonhomogeneity was necessary, at any rate for the charged corpuscular part of the radiation, in order to account for latitude and directional phenomena. However, this is a matter which it is not my purpose to discuss here.

W. F. G. Swann

Bartol Research Foundation,
Swarthmore, Pennsylvania,
January 7, 1935.

[1] W. F. G. Swann, Phys. Rev. **46**, 828 (1934).
[2] T. H. Johnson, Phys. Rev. **45**, 569 (1934).
[3] B. Rossi and S. de Benedetti, Ricerca Scient. **5**, 1 (1934).
[4] J. C. Street, as yet unpublished.
[5] C. G. and D. D. Montgomery, in a paper presented at the Pittsburgh meeting of the American Physical Society, December 27–29, 1934.
[6] R. D. Bennett, G. S. Brown and H. A. Rahmel, in a paper presented at the Pittsburgh meeting of the American Physical Society, December 27–29, 1934.

The Principal Limit of the Transmission of Solar Radiation by the Earth's Atmosphere in the Far Infrared

The absorption of solar energy by the Earth's atmosphere has been examined from 3μ to 21μ by means of a spectroheliometer with intermediate resolving power.

Very minute atmospheric windows on the long wave side of 13.5μ admit a negligible amount of energy. The principal infrared cut-off of the terrestrial atmosphere occurs at this point and is due to the lowest frequency fundamental (ν_2) of the carbon dioxide molecule. To the long wave side of $\nu_2(CO_2)$ the cut-off is occasioned principally by the pure rotation spectrum of the water molecule.

Numerous absorption bands due to CO_2, O_3 and H_2O were observed throughout the spectral limits recorded above. The spectrum is now being analyzed with high resolving power.

Complete details of the investigation will be reported in a forthcoming issue of this journal.

ARTHUR ADEL
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January 4, 1935.

On the Band Spectrum of Sulfur

In a recent letter, R. M. Badger,[1] using the wavelength of the lines given by Naudé and Christy,[2] derives a new analysis of the S_2 bands, which gives an internuclear distance for the lower state, agreeing with an empirical relation previously found by him. He has found also that the upper rotational levels of $v'=8$ [3] are perturbed and that in the lower state of this system the even rotational states are present, instead of the odd levels as found by Naudé and Christy, and as is also the case in the O_2 bands.

It should be pointed out that the overlapping of the S_2 bands makes an analysis of this system almost impossible, if one uses the combination principle as the only criterion. More than one combination was found in the process of the analysis given in reference 2. However, when other criteria were applied, such as the intensity of the lines within the branches, splitting of the lines of each branch into triplets at high values of K, etc., all the combinations were rejected as fortuitous except the one given in that paper.

It is difficult to determine, from the vibrational analysis of these bands,[3, 4] which of the vibrational levels are perturbed. However, we do know that predissociation occurs at $v'=11$. Naudé and Christy[2] have found that the rotational levels of $v'=8$, 9 and the lower levels of 10 are normal, while the higher levels of $v'=10$ are perturbed. Badger has found that the higher levels of $v'=8$ are perturbed, while all the others are normal. It is difficult to understand the presence of perturbation in the higher rotational levels of $v'=8$ and the absence of perturbation in the rotational levels of $v'=9$ and 10. Perturbations in $v'=8$ may be due either to the electronic state causing predissociation or to another similar state, but in either case we should have perturbations also in $v'=10$, especially since these rotational levels have been investigated to within approximately 100 cm^{-1} of the $v'=11$ vibrational level.

The number of branches, the intensity relation of the lines, and the splitting of the lines in the branches, clearly indicate that these bands are due to a $^3\Sigma-{}^3\Sigma$ transition. If Badger's analysis is correct, the lower $^3\Sigma$ state having only even rotational levels must be either $^3\Sigma_g^-$ or $^3\Sigma_u^+$. These two states cannot be derived from two normal S atoms. Therefore, since the products of dissociation are not known, the fact that only even rotational levels are present does not mean necessarily that the S atom is antisymmetric in the nuclei.

ANDREW CHRISTY

G-M Laboratories, Inc.,
Chicago, Illinois,
January 15, 1935.

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[1] R. M. Badger, Phys. Rev. **46**, 1025 (1934).
[2] S. M. Naudé and A. Christy, Phys. Rev. **37**, 490 (1931).
[3] The v' numbering used here is that given by Fowler and Vaidya, Proc. Roy. Soc. **A132**, 310 (1931), and is one unit greater than that given in references 2 and 4.
[4] A. Christy and S. M. Naudé, Phys. Rev. **37**, 1903 (1931).

Isotopes in Induced Radioactivity

It is interesting to note that the final stable products of the nuclear transformations resulting from alpha-ray bombardment in the cases so far reported, namely, $_{14}Si^{30}$, $_6C^{13}$, $_{13}Al^{27}$, $_{12}Mg^{26}$, $_{20}Ca^{44}$, $_8O^{17}$, are all the isotopes of rarest occurrence as shown in mass spectrum data.

	28	94%		12	99.75%					24	77.4%
Si	29	4%	C	13	.25%	Al	27	S	Mg	25	11.5%
	30	2%								26	11.1%

	40	98.6%		16	99.81%
Ca	44	1.4%	O	17	.03%
				18	.16%

In those nuclear transformations resulting from neutron bombardment reported by Fermi, the resulting stable atoms such as $_8O^{16}$, $_{12}Mg^{24}$, $_{16}S^{32}$, $_{24}Cr^{53}$, $_{26}Fe^{56}$, are the most frequently occurring isotopes.

	16	99.81%		24	77.4%		32	96%		50	4.9%		54	5%
O	17	.03%	Mg	25	11.5%	S	33	1%	Cr	52	81.6%	Fe	56	95%
	18	.16%		26	11.1%		34	3%		53	10.4%			
										54	3.1%			

These observations would seem to indicate that the transformations occurring in nature are, therefore, much more frequently of the neutron type.

T. R. WILKINS
L. S. SHNIDMAN

University of Rochester,
January 14, 1935.

The Raman Effect of Water Vapor

The Raman effect of water vapor has been observed with a Hilger E1 spectrograph by using Hg 2536 for excitation. The water was sealed in a quartz tube drawn into a horn at one end, and was illuminated by a water-cooled mercury arc. The tube with the water vapor was maintained at a temperature of approximately 135°C.

There was found but one Raman band shifted at its center 3654.5 cm^{-1} from the exciting line and extending for about 5 cm^{-1} on both sides of the center. It is not a sharp line for two much more intense and resolved mercury lines occupy only about the same distance on the microphotometer curve. Indeed, the limit of accuracy of the measurement is well within the half width of the line. Further than this there is no indication that the line is double, as was reported by Rank, Larsen and Bordner.[1]

As is well known the shift of the Raman line for ordinary water vapor is about 50 cm^{-1} greater than the corresponding fundamental frequency, while for heavy water vapor apparently the Raman line is close to the expected position of the fundamental.[2]

In an attempt to find an explanation for this discrepancy based on the location of the maximum of the vibration-rotation band, this band was worked out using the intensity factors for a symmetrical top[3] and using the positions derived from Mecke's[4] analysis of the infrared spectrum. The results indicate a strong group of lines corresponding to the Q-branch. Although the heavy water shows the greater relative intensity in this Q-branch the difference is not enough to account for its absence in ordinary water. The suggestion of Rank, Larsen, and Bordner[1] that the observed line consists of two members of the vibration-rotation band neglects the necessary presence of the rest of this band and appears to make use of lines forbidden by the selection rules.

A careful search was also made for a pure rotation band but none was found.

I wish to express my gratitude to Dr. W. V. Houston who has continually offered his aid and advice in carrying this problem out.

DAVID BENDER

California Institute of Technology,
December 24, 1934.

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[1] Rank, Larsen and Bordner, J. Chem. Phys. **2**, 464 (1934).
[2] L. G. Bonner, Phys. Rev. **46**, 458 (1934).
[3] Placzek and Teller, Zeits. f. Physik **81**, 209 (1933).
[4] R. Mecke, *et al.*, Zeits. f. Physik **81**, 313, 445, 465 (1933).

Proceedings of the American Physical Society

Minutes of the Los Angeles Meeting, December 21–22, 1934

THE 195th regular meeting of the American Physical Society was held in the auditorium of the Physics Department of the University of California at Los Angeles, California on Friday, December 21 and the morning of Saturday, December 22, 1934. The morning sessions ran from 9 to 12 and the afternoon session from 1:30 to 4:30. Thirty-one papers were presented on the regular programs and seven papers were presented on the supplementary program. About 150 members of the society attended the meetings. The society met at luncheon at the University Union on Friday noon. A business meeting was held during the Saturday morning session in which the society voted to hold the 199th regular meeting of the American Physical Society on the Pacific Coast in affiliation with the Pacific Division of the American Association for the Advancement of Science, at the University of California at Los Angeles about June 24–28, 1935. It was voted, to hold one of the sessions at the California Institute of Technology if it could be arranged. The question of the exact date of the meeting and of the possibility of holding some session at the California Institute of Technology was left to the discretion of the secretary with powers to act on behalf of the society. The abstracts of the papers follow.

LEONARD B. LOEB,
Local Secretary for the Pacific Coast

Abstracts

1. Chemical Identification of the Radioactive Element Produced from Carbon by Deuton Bombardment. L. N. RIDENOUR, D. M. YOST AND K. SHINOHARA, *California Institute of Technology.*—Because of the difference of half-lives of the radioactive elements produced by bombarding boron with alpha-particles (14 min.) and carbon with deutons (10.5 min.), which difference exists in spite of the fact that the products are presumably the same, a chemical investigation was undertaken to determine the nature of the radio-element produced in the latter case. Curie-Joliot and Joliot have given evidence that in the former case N^{13} results; the outcome of the present experiment indicates that the active element produced by bombarding carbon with deutons is also an isotope of nitrogen.

2. Gamma-Rays from Boron Bombarded with Deutons. H. R. CRANE, L. A. DELSASSO, W. A. FOWLER AND C. C. LAURITSEN, *California Institute of Technology.*—The energy spectrum of recoil electrons produced by the gamma-rays from boron bombarded with deutons has been studied by means of a Wilson cloud chamber operating in a magnetic field of 1000 gauss. The gamma-radiation was found to consist of components of at least five different energies, and these are in good agreement with the differences in energy of the proton groups, and with the known excitation levels in some of the nuclei which result from the transmutation.

3. The Disintegration of Nitrogen by Neutrons. FRANZ N. D. KURIE (*National Research Fellow*), *University of California.*—Measurements made on 29 Wilson cloud chamber photographs of the disintegration of nitrogen by neutrons are presented and discussed. It is shown that the loss in kinetic energy can be satisfactorily accounted for by postulating the momentary production of a radioactive nitrogen (N^{16}) by a radiative capture of the neutron. This nitrogen disintegrates with the emission of α-particles so that the half-life is on the Gamow theory around 10^{-20} sec. A distinction is thus made between nuclear transformations in which the energy absorbed is a constant (such as in the case of the disintegration of nitrogen by α-particles) and those in which the proper disintegration energy E is a constant. Disintegrations caused by neutrons are, as far as the data from cloud chamber measurements go, all of this latter type. For nitrogen E is found to be 3.1 mv. The scatter of the values of E is probably all due to be attributed to experimental error but may in part be due to the short life of the radioactive N^{16}. The energy level from which the α-particle leaves the N^{15} nucleus is roughly identified with the resonance level through which an α-particle may enter a B^{11} nucleus in the reverse reaction. A mass for the radioactive N^{15} of 15.0166 is proposed on the basis of the mechanism here discussed. The data of other workers on the transmutation of oxygen, fluorine and neon are reviewed in the light of these considerations and lend support to them. The values found for E are nearly the same for all of the four elements for which data exist.

4. The Energy of the Neutrons Emitted from Beryllium when Bombarded by Deutons. J. R. RICHARDSON AND FRANZ N. D. KURIE (*National Research Fellow*), *University of California.*—The energy of the neutrons emitted from

beryllium when bombarded by deutons was studied by measuring the ranges and angles of projection of helium recoil atoms in a cloud chamber placed nearby. It was found, in a separate series of experiments, that 90 percent of the neutrons arrive at the chamber without having been scattered. Hence one can take the line drawn from the source to the point from which the recoil atom begins its flight as the neutrons' path. The beginning and end of the helium recoil track not being distinguishable in general, the beginning was taken as that end which gives the minimum angle of projection. The final spectrum was corrected for the effect of the solid angle subtended by the chamber. One finds then a spectrum extending from below 1 mv through a maximum around 2 mv on up to 10 mv and perhaps beyond. It is difficult to set the upper limit of the energies because of the influence of the scattered neutrons. The decline in numbers between 2 mv neutrons and 10 mv neutrons is gradual. The maximum at 2 mv is perhaps not real since it was difficult to measure tracks of lengths smaller than those corresponding to about a 1 mv neutron.

5. Energy of the Neutrons from the Disintegration of Beryllium by Deutons. T. W. BONNER (*National Research Fellow*) AND W. M. BRUBAKER, *California Institute of Technology*.—Beryllium has been disintegrated by 900,000 e.v. deutons with the Lauritsen and Crane apparatus. The energies of the neutrons produced in this disintegration have been determined from the range of recoil protons observed in a Wilson cloud chamber which was filled with CH_4 at about 14 atmospheres pressure. The maximum of the proton ranges was found to be 28 cm which correspond to neutrons of maximium energy 4.5 m.e.v.

6. Transmutations of Aluminum by Deutons. EDWIN MCMILLAN AND ERNEST O. LAWRENCE, *University of California*.—Aluminum bombarded by 2.2 mv deutons is found to emit neutrons, protons, and alpha-particles, presumably accompanying the formation of Si^{28}, Al^{28} (radio aluminum), and Mg^{25}, respectively. The alpha-particles are very few in number and have a range of about 6.5 cm. The protons have a very complex spectrum of energies. By using a target of thin Al foil and a Wynne-Williams counter biased sufficiently to resolve groups 4 cm apart, it was possible to identify strong proton groups at 10 and 22 cm, weaker ones at 30 and 54 cm, and still weaker unresolved groups between the latter two and extending out to the maximum range of 62 cm. The radioactive product, shown chemically to be an aluminum isotope, emits negative electrons and a strong gamma-ray with a half-life of 153 sec. The maximum range of the electrons is about 0.95 g/cm^3 of Al. The excitation curve of the radioactivity follows the Gamow nuclear penetration function very closely.

7. Transmutations of Nitrogen by Deutons. ERNEST O. LAWRENCE, EDWIN MCMILLAN AND MALCOLM C. HENDERSON, *University of California*.—Nitrogen bombarded by 1.3 mv deutons emits neutrons, protons and alpha-particles. The neutrons are involved probably in the reaction in which radio-oxygen (O^{15}) is formed. The protons and alpha-particles are probably emitted in the formation of N^{15} and C^{12}, respectively. There are two proton groups of ranges 25 and 85 cm, indicating a mass of 15.0049 for N^{15} and the frequent emission of a 4.6 mv γ-ray from N^{15}. There are three alpha-particle groups of ranges 6.7, 7.6 and 12.5 cm. The energy of the long range group agrees with that calculated from the mass spectrographic values for C^{12} and N^{14}, and the two shorter range groups suggest the existence of excited levels in C^{12} at 4.0 and 4.8 mv.

8. Photoelectric Effect and Spark Mechanism. A. M. CRAVATH, *University of California*.—To start a spark some additional mechanism is required in addition to the well known ionization by electron collision. Several mechanisms have been discussed but heretofore none has been shown to actually occur to the necessary extent under ordinary static breakdown conditions. The photoelectric effects produced by the radiation from electron currents in air at atmospheric pressure are being measured at low current densities and at fields in the breakdown range. There are at least two components of radiation. The first has an absorption coefficient in air of about 2 cm^{-1} and would release a photoelectric current 10^{-5} times (in order of magnitude) the current produced by electron collision if all the radiation struck brass. The second component has an absorption coefficient in air of about 10 cm^{-1} and is more effective in ionizing air than in releasing photoelectrons from brass. In order of magnitude, one such photo-ion is produced for every 10^4 ions produced by collision when all the radiation is absorbed in air. Fluorite stops both components. Hence they fall in the oxygen transmission region centering around 1100A. Intensities and absorption coefficients are of the right order of magnitude to explain the sparking potential for parallel electrodes in air at one atmosphere for gaps from 0.01 to 10 cm.

9. An Investigation of the Magneto-Optic Method of Chemical Analysis. H. G. MACPHERSON, *University of California*.—An apparatus similar to that used by Allison in his magneto-optic method of chemical analysis was set up in an effort to verify the existence of the sharp Allison minima. Many visual observations were made, but only occasionally did readings of possible minima occur in more than random groupings. Where these apparent minima did occur, it was thought that they could be explained as being due to such factors as sticky places on the trolley felt by the hand on the hand wheel control. When a motor control was used on a later apparatus, the distribution of readings of possible minima was no more than a chance distribution. Objective tests were made of the variation of intensity of light with trolley position by a photographic method. In this photographic method the effect of spark fluctuations was eliminated by comparing the intensity of the light passing through the cells with that of a comparison beam direct from the spark. Individual runs by this method showed no minima and were good to 3 percent. When several runs were averaged, the resultant intensity curve showed no variations greater than 1 percent. Eye tests showed that the writer could not have detected an intensity change visually of less than 3 percent on the magneto-optic apparatus. Thus these results definitely indicate that the minima

supposedly characteristic of chemical substances at times seen by the writer have no objective reality and hence no real significance.

10. Ionization of Inert Gases by Positive Alkali Ions with a Balanced Space-Charge Method. ROBERT N. VARNEY, *University of California.*—The study of ionization of inert gases by collisions of alkali ions reported last summer has been extended to include krypton, xenon, helium and methane. The method of detecting the newly formed ions is designed to be entirely unaffected by secondary electrons liberated from the walls. The ionization is allowed to take place in a cylinder which is already carrying a space-charge limited current of electrons. The positive ions formed tend to neutralize the space-charge, by the process discovered by Kingdon, in such a manner that an additional surge of about 50,000 electrons flows for each positive ion produced in the region. A second cylinder, identical with the first and carrying also a space-charge limited current of electrons but closed to the positive ions, is used to balance out spurious fluctuations in the electron current. The recent results indicate the following ionization potentials for the various alkali ions used as ionizers:

	Kr	Xe
K^+	72	115 volts
Rb^+	103	151

No ionization was observed below 500 volts either in methane or in helium. The possible similarity in electron configuration of argon and methane led to the study of the latter, but the intense ionization of argon was not duplicated.

11. Elastic Scattering of Fast Electrons in Mercury and Agreement with Mott's Theory. W. E. STEPHENS, *Washington University of St. Louis.*—Jordan has recently reported good agreement between Mott's theory and the experimentally measured angular distribution of elastically scattered electrons for 2000 volts in mercury in the angle range 0° to 42°. In view of Morse's criterion, that the minimum energy for which Mott's equations are accurate is of the order of $50Z^2$ (Z is the atomic number), we should not expect good agreement much below 320,000 volts in mercury. In preliminary experiments, with an apparatus developed to record the angular distribution of scattered electrons photographically, we have found a distinct maximum near 112° at 2000 volts in mercury. Since Mott's theory gives a monotone curve, we can conclude that there is not good agreement over the whole angular range for 2000 volts in mercury. In the apparatus used, a beam of fast electrons was shot through a molecular beam of mercury. A retarding potential was used to stop the inelastically scattered electrons and an accelerating potential served to increase the blackening effect of the elastically scattered electrons at the film.

12. An Automatic High Pressure Wilson Cloud Chamber. W. M. BRUBAKER AND T. W. BONNER (*National Research Fellow*), *California Institute of Technology.*—A high pressure Wilson Cloud Chamber of new design has been built for the study of recoil protons from neutrons. The apparatus is entirely automatic in operation. It can be used at any pressure under 20 atmospheres. Illumination for photographing the proton tracks is obtained from a 2000-watt photo-flood lamp.

13. Polarization Effects in the Hilger E1 Quartz Spectrograph. JOSEPH W. ELLIS AND JOSEPH KAPLAN, *University of California at Los Angeles.*—Serious limitations are encountered in the use of the Hilger E1 spectrograph whenever the light is polarized or partly polarized. If the light is plane polarized in any plane except the vertical or horizontal the visible spectrum shows closely spaced striations whose visibility and number reach maxima when the plane of polarization makes a 45° angle to the vertical. At this angle there occur four positions of zero visibility. These striations are produced in the following way. The small crystalline quartz reflecting prism near the slit acts as a 300*th*-to-500*th* wave-plate. The quartz collimating lens rotates the planes of polarization to such angles that the waves acted upon in half-wave plate fashion and whole-wave plate fashion are parallel to or at right angles to the plane of incidence of the dispersing prism. Maxima and minima of intensity result and these interchange as positions of zero visibility are passed corresponding to polarizations at 45° angles to the plane of incidence. If the original light is polarized in a vertical or a horizontal plane, then the reflecting prism has no wave plate action, no striations appear and broad minima and maxima of intensity occur with the spacings of the former visibility minima.

14. New Band Systems in Nitrogen. JOSEPH KAPLAN, *University of California at Los Angeles.*—Spectra, taken on a Hilger E31 quartz spectrograph at pressures varying continuously from about 10 mm to lower values, are shown. In these photographs, the new Appleyard-van der Ziel system and the two new ultraviolet systems discovered by the author become stronger as the pressure lessens. The Lyman-Birge-Hopfield bands however, which are very strong at high pressures, become weaker and finally almost disappear at the lowest pressure at which a discharge is still possible. The first-negative bands of N_2^+, which are very strong in the tube at high pressures, also gradually become weaker as the pressure goes down. This is one reason for believing that the three band systems are emitted by the neutral nitrogen molecule. The fact that all three systems become stronger as the pressure is lowered indicates that they have similar origins. In fact, all three systems have the same lower electronic level, and two of the three systems originate on two levels of the set discovered in absorption by Hopfield and shown by him to fit a Rydberg series formula. Many other new bands are present on the spectrograms and some of them have been tentatively grouped together. A slide is shown in which the recent changes in our knowledge of the spectrum of the nitrogen molecule are summarized.

15. The Optical Properties of Magnesium Oxide. R. T. BRICE AND JOHN STRONG, *California Institute of Technology.*—The index of refraction of MgO has been measured for a number of wavelengths in the visible and ultraviolet, $N_C = 1.733$, $N_F = 1.747$. The dispersion is 55.3; the trans-

mission limit in the ultraviolet is about 2200. The substance is found reasonably suitable for use with quartz and fluorite to form an achromatic triplet for the ultraviolet. Windows have been made of MgO for use in high-temperature furnaces and tested with lithium, sodium, potassium and calcium and found to withstand etching by these metals better than windows of other materials. MgO crystals may be obtained commercially up to about three centimeters square by one centimeter thick. It is possible that larger ones may be obtained if suitable care is taken to form them.

16. Fine Structure and Hyperfine Structure of Doubly Ionized Beryllium. S. S. BALLARD, O. E. ANDERSON AND H. E. WHITE, *University of California.*—The spectrum of doubly ionized beryllium is being investigated for the purpose of determining the fine structure as well as the hyperfine structure of the ^3P terms. The fine structure intervals in $1s2p$, ^3P as calculated theoretically by Heisenberg and others should not follow the Lande interval rule. With the small atomic number 4 and mass number 9 one would predict a nuclear spin of $I=\frac{1}{2}$ for the beryllium nucleus, and attribute it to a single unbalanced neutron. Since the magnetic moment of the neutron appears from other experiments to be quite small, relatively narrow hyperfine structure is to be expected even in the most favorable terms and spectrum lines of beryllium. The ionized spectrum has been excited by a direct current vacuum spark with 60,000 volts and a capacity of 0.3 mfd. The lines arising from the transition $1s2s$, $^3S_1-1s2p$, $^3P_{0,1,2}$ are observed at λ3720. Two lines of the triplet, $^3S_1-^3P_2$ and $^3S_1-^3P_0$, are observed to fall practically together as predicted, and the hyperfine structure, although not resolved, is found to be quite narrow.

17. The Nuclear Magnetic Moment of Cobalt. KENNETH R. MORE, *University of California.*—A study of the hyperfine structure patterns in the Co I spectrum has led to a value of 7/2 for I (K. R. More, Phys. Rev. **46**, 470 (1934)). This study has been extended to include a determination of the nuclear magnetic moment. The absolute hfs. splittings of the $3d^74s4p$ ^4D terms are found from the splittings of the lines of the $3d^74s$ $^4P-3d^74s4p$ ^4D multiplet. The relative splittings of the ^4D levels are not in good agreement with those predicted by the Bacher-Goudsmit equations on the assumption that all the splitting is due to the coupling of the moment of the $4s$ electron with the nuclear moment. Better agreement is obtained by including the interaction of the orbital moment of the d electrons with the nuclear moment. With the assumption that part of the interaction is due to the $3d$ electrons, the coupling constant a' of the $4s$ electron is found to be 0.13 cm^{-1}. The nuclear g-factor is found, on the substitution of this value of a' in the equations given by Goudsmit (Phys. Rev. **43**, 636 (1933)), to be 0.77. This leads to a value of 2.7 nuclear magnetons for the nuclear magnetic moment of cobalt.

18. The Transfer of Translational and Vibrational Energy in Oxygen as Influenced by Small Impurities of Water or Ammonia Vapor. VERN O. KNUDSEN AND LEONARD OBERT, *University of California at Los Angeles.*—Previous experiments in this laboratory, based on reverberation measurements, have shown that at audible frequencies the absorption of sound in O_2 is greatly increased by the addition of small impurities of such gases as H_2O and NH_3. The present work, based on intensity measurements, extends these experiments to frequencies as high as 40,000 cycles. Kneser has shown that the results at audible frequencies are in good agreement with the recent theory of sound dispersion and absorption, provided the rate of adjustment of the vibrational energy of the O_2 molecule is strongly influenced by the presence of small amounts of other gases. Conversely, absorption measurements become useful for investigating energy transitions in molecular collisions. For example, it is found that the reaction rate k_{10} (number of transitions from the excited to the normal state per molecule per second) for O_2 is almost a linear function of the concentration of small impurities of NH_3, but is largely a quadratic function of the concentration of small impurities of H_2O. Although the results are in good agreement with Kneser's formula at frequencies below 20,000 cycles, the observed absorption at higher frequencies is in excess of the value given by this formula.

19. Experimental Features of the Spectrum of Samarium. ARTHUR S. KING, *Mount Wilson Observatory.*—The spectrum of samarium is of interest as material for term analysis, this element being near the middle of the rare-earth group, the end numbers of which have received most attention from analysts. In the present work, about 4500 lines from λ2900 to λ8700 have been given temperature classification. Over 400 of these fall in classes I and II, arising from low atomic levels. Many neutral lines not previously measured appear in the furnace spectrum. The lines of Sa II, which are of astrophysical interest, are selected by a comparison of furnace, arc and spark spectra. Since many of these singly-ionized lines appear in the furnace, the classification indicates their relative atomic levels in Sa II. The spark spectrum shows also some lines of Sa III in the region examined. Hyperfine structure appears in many samarium lines, especially those of Sa II, and is most frequent in the red and infrared. Those which are resolved are doublets, with the violet component stronger, and various degrees of separation up to 0.43 cm^{-1}. The nuclear mechanical moment indicated is therefore $(1/2)\cdot(h/2\pi)$; though an examination of samarium lines under high resolution is needed for the close patterns and to test for a possible influence of the known isotopes.

20. Spectrum of Aluminum Vapor Emitted by a Tungsten Coil in Vacuum. JOHN STRONG AND E. GAVIOLA, *California Institute of Technology.*—If a tungsten coil charged with aluminum is brought to incandescence in a vacuum of the order of 10^{-5} mm Hg, it evaporates a cloud of metal, which has been observed to emit a bluish-green light. The potential drop across the coil ranges from 10 to 40 volts. The emitted light has been photographed with a glass and with a quartz spectrograph and found to be mainly a line spectrum containing Al I, Al II and W lines. The following lines have been identified so far:

Al I		Al II		W	
3962	2373	3901	2631	4867	3376
3944	2372	3587	2369	4843	3077
3093	2367	3446	2321	4660	3024
3082	2269	3444		4365	
2660	2263	3057		4302	
2652	2258	3050		4295	
2575	2210	2816		4103	
2568	2204	2669		4074	
2378				4009	

The excitation seems to be produced by collisions with the electrons emitted by the incandescent filament and accelerated by the potential gradient between one end of it and the walls of the container. The intensity ratio of the lines is not the same as in the usual metal arc. Furthermore while the lines starting in the higher levels of Al are diffuse in the arc, they are notably sharp in the vacuum source. Displacements of some vacuum lines are indicated by the spectra. The presence of the W lines shows that part of the coil dissolves in the melting Al and is carried away while it evaporates.

21. The Spectrum of AsO. F. A. JENKINS AND L. A. STRAIT, *University of California.*—The band spectrum of AsO has been photographed in the second order of a 21-foot grating, by using as a source a high-frequency discharge through As_2O_3 vapor and helium in a sealed-off quartz tube. Two systems of double-double headed bands are observed, for which the Q heads are represented by the following equations:

$$\text{System } A: \quad \nu = \begin{cases} 31{,}655.8 \\ 30{,}631.1 \end{cases} + 683.8(v'+\tfrac{1}{2}) - 9.42(v'+\tfrac{1}{2})^2 - 966.6(v''+\tfrac{1}{2}) + 4.92(v''+\tfrac{1}{2})^2,$$

$$\text{System } B: \quad \nu = \begin{cases} 40{,}410.5 \\ 39{,}386.8 \end{cases} - 966.6(v''+\tfrac{1}{2}) + 4.92(v''+\tfrac{1}{2})^2.$$

The analysis of system A disagrees with that recently given by Shawhan and Morgan, and requires that the common final state be an electronic doublet, there being no doubling in the initial state of either system. An analogous situation exists for PO, in which the longer wavelength system (Geuter's A) shows a doubling of 226 cm^{-1}, agreeing with that of Geuter's B system, according to unpublished work by one of us. The fact that we observe only the $v'=0$ progression in system B of AsO, and that the doublet components are very different in intensity, the high-frequency component being less intense, indicates predissociation in the upper state of this system. Bands with $v'>0$ have been observed under lower dispersion with other modes of excitation by de Watteville and by Shawhan and Morgan. Accepting the values $\omega_e'=1098$, $x_e'\omega_e'=6$ given by the latter authors, the electronic terms of the upper state become 39,862.0 and 38,838.3 cm^{-1}.

22. An f.l. Quartz Spectrograph. SINCLAIR SMITH, *Mount Wilson Solar Observatory.*—The novel feature of this spectrograph is a Schmidt camera consisting of a quartz correcting plate and four inch radius of curvature aluminized mirror. Having a two-inch aperture and a two-inch focal length the instrument is obviously very fast. An aluminized off-axis parabolic mirror is used for a collimator and the dispersion is produced by a Cornu quartz prism. Although the field is not flat, the instrument gives excellent definition from below λ3000 to about λ4500.

23. Intensities of X-Ray Reflection from Bi Crystals Between 25° and 530° Abs. R. B. JACOBS AND A. GOETZ, *California Institute of Technology.*—The integrated intensities of Mo $K\alpha$-radiation from (111) of highly purified Bi crystals have been measured between the boiling point of hydrogen and the melting point of Bi for the 2nd, 3rd and 5th order. It was found that: (1) Between 25° and 480° abs the integrated intensities follow the Debye-Waller function: $I/I_0=e^{-kT\sin^2\theta}$ with better precision than was found by previous authors on cubic crystals (NaCl, Al etc.) for higher temperatures and within smaller ranges of total energy variation, as far as $I/I_0=f(T)$ is concerned. This proves the validity of the above law in the T^3-region. (2) The comparison of the intensities among the different orders proves a good agreement for $I/I_0=f(\theta)$, although the original theory does not include the hemihedral hexagonal system to which Bi belongs. (3) For the last 40° before fusion a definite deviation from the law takes place, as $d(I/I_0)/dT$ (<0) begins to decrease and to reach even positive values, indicating a rearrangement in the sense of a larger degree of geometrical order within the crystal before fusion.

24. The Phenomenon of Supercooling. ALEXANDER GOETZ, *California Institute of Technology.*—The phenomenon of super-cooling in metals is interpreted as group-phenomenon (A. Goetz, Zeits. f. Krist. **A89**, 310 (1934); Proc. Roy. Soc. Intern. Conference of Phys. 1934) as due to the fact that the transition into the rigid crystalline state has to be anteceded by a paracrystalline mesophase. It can thus be concluded that supercooling is the more likely the more the lattice of the crystal differs from a statistical (close packed) configuration and the more groups of paracrystalline qualities have been destroyed in the melt. Experiments prove that for metals with irregular lattices like Ga and Bi the supercooling can be induced over large ranges of temperature by superheating the melt or by surface forces acting upon sufficiently thin metallic layers. The beginning of the mesophase is determined for Bi and Ga to 10–12° above the melting point and the size of a group estimated to 10^{-4} cm.

25. A Precision Magnetic Field Standard. FRANK G. DUNNINGTON, *National Research Fellow, California Institute of Technology.*—The determination of e/m being made by a new deflection method (Phys. Rev. **43**, 404 (1933)) is limited in accuracy by the precision of the magnetic field. To reduce this uncertainty a very carefully built solenoid has been constructed. A heavy copper tube which is threaded on the outer surface has baked upon it a thin layer of bakelite for insulation. New threads are then cut in the Bakelite (over those in the copper) leaving a continuous insulating layer about 0.004 inch thick. The copper wire wound in these threads was made especially for the purpose, commercial wire not being sufficiently round. The advantages of this design are: coefficients of expansion of wire and form are the same (not true with a marble form);

the Bakelite provides a firm machinable insulation which cannot appreciably change the coil dimensions by moisture absorption; and the geometry is completely observable since bare wire is used. An accuracy of a few parts in 100,000 is attainable for a field of a few gauss. The method used in precisely comparing two magnetic fields will be described, including the precautions necessary in the potentiometer circuit and the establishment of the standard of voltage.

26. A Null Method Photoelectric Photometer. HIRAM W. EDWARDS, *University of California at Los Angeles.*—Two photoelectric cells (RCA No. 868) are selected which have very nearly similar characteristics. The voltage on one cell is adjusted so that the anode currents through the two cells are identical when the cell surfaces are equally illuminated. A single galvanometer links the two electrical circuits with the two anode currents through it in opposition thereby producing a zero deflection when the intensities of the illumination are equal. The instrument shows a high degree of sensitivity with a good galvanometer, is inexpensive and is very easy to operate. In an application of this photometer to a measurement of relative intensities of two light sources, it is, of course, necessary to bear in mind the peculiarities of the cell response to the spectral distribution of energy in the sources.

27. Equations of State and Thermodynamic Functions for Substances with Variable Specific Heat. W. P. BOYNTON, *Oregon State College.*—In thermodynamical discussions it is often, though not necessarily, assumed that specific heat at constant volume is constant. From the first and second laws of thermodynamics it can be shown that

$$C_v = T\int \frac{\partial^2 p}{\partial T^2} dv + f(T),$$

where $f(T)$ is a function of integration. This conclusion has been applied to a highly generalized equation, of which many well known equations of state are special cases, and expressions derived for the specific heat at constant volume, energy and entropy. Any equation of state may be expected to fit experimental data only over a limited field, and intrinsically discontinuous changes in state must necessitate a change in constants, if not in the form of the equation. The author discusses the possibility of bringing values of energy and entropy derived from such an equation into conformity with the third law.

28. Townsend Coefficients in Nitrogen. D. Q. POSIN, *University of California. Introduced by Leonard B. Loeb.*—Carrying on the investigation of the Townsend coefficients for ionization by collision by electrons which had been completed for air by F. H. Sanders (Phys. Rev. **41**, 667 (1932); Phys. Rev. **44**, 1020 (1933)) in this laboratory, measurements have been extended to nitrogen. The purpose of this work is to determine these coefficients in a molecular gas, which does not react with the electrodes, in order to establish the values of these coefficients and their behavior, with the hope of detecting an influence on the value of the so-called positive ion coefficient β due to electrode material. In view of the fact that no data exist at present for nitrogen at low values of X/p, investigations were carried on in pure dry nitrogen using brass electrodes and the technique of Sanders with the results given in the table.

x/p	α	α/p	x/p	α	α/p
46	1.43	0.0143	34	0.714	0.00286
42	0.85	.0085	32	.50	.0020
40	.80	.008	28	.238	.000576
38	.77	.00513	26	.175	.00035
36	1.18	.00472	24	.0454	.000091

29. A Foucault Pendulum with Constant Amplitude. R. M. LANGER, *California Institute of Technology.*—A Foucault pendulum of period 7.1 sec. and an amplitude of about 10 degrees is supplied with energy from an electromagnet during part of each upswing. The electromagnet devised by J. T. Barkelew is axially symmetrical and exerts a radial force on an armature attached to the pendulum suspension about 1 foot below the plane of the crossed knife edges on which the pendulum is supported. The force on the armature is zero at the center and increases gradually with displacement from the center. The amount of energy supplied to the pendulum can be varied by changing the time during which the electromagnet is activated as well as by varying the current. The impulses are timed by the pendulum itself. When it reaches the vertical the circuit is closed by a photoelectric device. At a fixed time later a photo-cell operates relays which open the circuit. It takes less than 20 watts to maintain constant amplitude of the pendulum although ten times as much could be furnished easily by this device. No appreciable change in motion of the bob results from the fairly weak and gradual impulses supplied in this way. The pendulum, designed largely by the late E. H. Kurth, is installed at the Griffith Observatory in Los Angeles.

30. Propagation of Micro-Radio Waves. PAUL S. EPSTEIN, *California Institute of Technology.*—As recent experiments by Marchese G. Marconi showed, micro-waves (of 50 cm wavelength) can be used for communication over distances several times larger than the range of rectilinear visibility. The question arises to what extent this is due to atmospheric influences. To answer this, the theory of propagation of such waves in the absence of any atmosphere was developed. Marchese Marconi's observations are not quantitative, qualitatively they are in agreement with the intensities calculated from formulas completely neglecting the influence of the atmosphere.

31. Relative Measurement of the Standing Wave System in a Mechanically Blown Flute Tube. R. W. YOUNG AND D. H. LOUGHRIDGE, *University of Washington.*—Data are presented showing the air motion within a mechanically blown flute tube. The exploring probe consists of a short heated platinum filament welded between two long wire supports so mounted that the probe may be drawn to any position within the tube. The average resistance changes of the filament are determined by a Wheatstone bridge,

and the periodic change by a suitably connected tuned audio-frequency amplifier. Measurements show an enormous cooling near the mouth end, indicative of a turbulent motion which soon dies off as the distance from the mouth increases. Beyond this, sinusoidal standing wave systems are observed, terminating in a sort of exponential decrease in velocity amplitude beyond the open end of the tube.

32. A High Speed Oil Diffusion Pump. HIRAM W. EDWARDS, *University of California at Los Angeles.*—The peculiarities of design in this pump are, the use of streamlines in regions of high pressure and the introduction of small angle conical surfaces for baffles in the regions of lower pressures. The conical baffles are particularly effective in preventing oil vapor from entering the chamber to be evacuated and at the same time in offering a minimum of impedance to the flow of gas through the pump. A three inch pump with this design and operating on a Western mineral oil especially prepared for it in this laboratory has shown a pumping speed in excess of 50 liters per second at a pressure of 1.0×10^{-4} mm.

33. A Comparison of the Rotary Voltmeter and the Sphere Gap up to 830 Kilovolts. JOSEPH E. HENDERSON AND WILBUR H. GOSS, *University of Washington, and* JOHN E. ROSE, *Tumor Institute of the Swedish Hospital, Seattle.*—A rotary voltmeter similar to that described by Kirkpatrick has been built and utilized up to 830 kilovolts peak. The calibration was made using an 8000 volt d.c. generator. The instrument has proved to be a practical instrument for both voltage and wave form measurement in this region. A comparison of the voltages so measured with those indicated by a 75 cm sphere gap, positive sphere grounded, shows that the A. I. E. E. sphere gap standards need revision downward, the error being about 7 percent at the highest voltage measured. The agreement between the rotary voltmeter and recent measurements of Meador, who utilized a crest voltmeter and transformer coil, is within the experimental error of both measurements.

34. An Analysis of the Diurnal Variation of the Earth's Potential Gradient. JOSEPH G. BROWN, *Stanford University.*—A direct analysis of the diurnal variation of the potential gradient has been made from all available data. The unitary, or universal time component has been obtained from the ocean and polar observations. This has been subtracted from the observed variations to obtain the local variations. The local variations have been separated into two components. One component has the same form as the inverse of the diurnal variation of the virtual height of the ionosphere and is similar at all stations. The other component is a day-time depression which varies in magnitude and time of occurrence at the different stations and is assumed to be due to strictly local factors. While this analysis does not pretend to be exact, it is believed that it suggests the correct causes of the diurnal variation, *viz.:* an oscillation of the Earth's fluid as a unit, probably due to thunderstorms as suggested by Whipple; a wave of approximately simple harmonic form and 24-hour period, probably due to variation in height of the ionosphere, produced by the Sun's radiation; and a local depression, probably due to meteorological changes which affect the conductivity and space-charge distribution in the lower atmosphere.

35. A New System of Nitrogen Bands. JOSEPH KAPLAN, *University of California at Los Angeles.*—Four new bands, whose wavelengths are 2242, 2316, 2392 and 2472A, have been observed in the bulb of the discharge tube in which the Vegard-Kaplan bands were discovered. These bands were observed only at the lowest pressure at which a discharge could be produced. As the pressure was lowered the Vegard-Kaplan bands grew weaker and this new system increased in intensity. The van der Ziel and the two new ultraviolet systems reported by the author, were absent in this portion of the tube but were intense in the narrow part, although this new system is present in the narrow portion of the tube also. The bands degrade to the violet and are similar in appearance to the van der Ziel and the two other ultraviolet systems. All four systems increase in intensity with decreasing pressure. The lower state of this new system seems to be identical with the lower state of the three systems mentioned above, and it is probably a $^1\Sigma_g$ level since the initial state of the van der Ziel system is a $^1\Sigma_u$ level. If we assume that the lower state is identical with that of the van der Ziel bands, the four bands above are the (0,4), (0,5), (0,6) and (0,7), respectively.

36. Preliminary Report on the Experimental Method of Detecting Anomalous Dispersion of Sound in Air in the Audible Range as a Function of Frequency and Humidity. LEO P. DELSASSO AND JOHN H. MUNIER, *University of California at Los Angeles.*—In the work of H. O. Kneser on the dispersion of sound in gases, the velocity of sound should show an increase in a certain frequency range, this range depending upon the particular properties of the gas in question. The apparatus has just been completed which should permit the dispersion of sound to be detected. The method used is in general that of Michelson and Hebb with a number of refinements which have been made to increase the accuracy to the highest degree.

37. The Mechanism of the High Velocity of Propagation of Lightning Discharges. A. M. CRAVATH AND L. B. LOEB, *University of California.*—Observations by Schonland and Collens (Proc. Roy. Soc. **A143**, 654 (1934) with Boys' camera show that the luminous tip of the leader stroke of the lightning discharge advances with a high velocity sometimes exceeding 3×10^9 cm per second. From the fact that electrons traveling 10^9 cm per second produce about 6000 new electrons per cm of actual path and that 6000 new electrons per cm in the direction of the field (i.e., $\alpha=6000$) requires 4×10^6 volts per cm shows that to give the electrons a velocity in the direction of the field of 10^9 cm per second would require a field exceeding 4×10^6 volts per cm even at the tip of the stroke. The fields, and therefore the electron velocities, are certainly far less than this value. Accordingly the velocity of the tip greatly exceeds the velocity of the electrons in the tip. It is possible

to account for this velocity as follows: Calculations based on justified assumptions concerning the conditions known to exist in a lightning stroke show that if the field just ahead of the tip averages 10^5 volts per cm for about one centimeter, ionization by collision by the electrons present in the gas before the stroke would be great enough to advance the tip at the observed rate. Such a field is found not too high to be consistent with the low conductivity of the leader path. In this way a propagation of the leader stroke of a velocity many times higher than the velocity of the electrons can be attained.

38. Forces Between Nuclear Particles. W. V. HOUSTON, *California Institute of Technology.*—The interaction between a nucleus and a positive particle is usually schematized by a potential energy which is that of a coulomb field into distances of the order of 10^{-12} cm and which falls off rapidly toward a minimum at the center of the nucleus. This minimum may be either positive or negative. A number of nuclear phenomena can be accounted for roughly as due to the passage of the positive particles through the potential barrier thus postulated. It is perhaps worth while to point out that very similar calculations can be made, on the basis of a purely repulsive potential, by making use of the negative energy levels which are characteristic both of Dirac's theory and the scalar relativistic equation. As soon as the potential energy is greater than $E+mc^2$ the solutions of the wave equation are oscillating. Thus positive particles could exist inside the nucleus in a state of positive total energy but negative kinetic energy. They could then leak through to the outside in the usual way. If a purely coulomb field is used, the lifetime of such a state is very long. If the potential is assumed to rise very rapidly at about the usual nuclear radius it is possible to get the ordinary formulae for radioactive decay which depend upon the radius assumed.

AUTHOR INDEX TO ABSTRACTS OF THE LOS ANGELES MEETING

Anderson, O. E.—see Ballard

Ballard, S. S., O. E. Anderson and H. E. White—No. 16
Bonner, T. W. and W. M. Brubaker—No. 5
—— see Brubaker
Boynton, W. P.—No. 27
Brice, R. T. and John Strong—No. 15
Brown, Joseph G.—No. 34
Brubaker, W. M. and T. W. Bonner—No. 12
—— see Bonner

Crane, H. R., L. A. Delsasso, W. A. Fowler and C. C. Lauritsen—No. 2
Cravath, A. M.—No. 8
—— **and L. B. Loeb**—No. 37

Delsasso, L. A.—see Crane
Delsasso, Leo P. and John H. Munier—No. 36
Dunnington, Frank G.—No. 25

Edwards, Hiram W.—Nos. 26 and 32
Ellis, Joseph W. and Joseph Kaplan—No. 13
Epstein, Paul S.—No. 30

Fowler, W. A.—see Crane

Gaviola, E.—see Strong
Goetz, Alexander—No. 24
—— see Jacobs
Goss, Wilbur H.—see Henderson

Henderson, Joseph E., Wilbur H. Goss and John E. Rose—No. 33
Henderson, Malcolm C.—see Lawrence
Houston, W. V.—No. 38

Jacobs, R. B. and A. Goetz—No. 23
Jenkins, F. A. and L. A. Strait—No. 21

Kaplan, Joseph—Nos. 14 and 35
—— see Ellis
King, Arthur S.—No. 19
Knudsen, Vern O. and Leonard Obert—No. 18
Kurie, Franz N. D.—No. 3
—— see Richardson

Langer, R. M.—No. 29
Lauritsen, C. C.—see Crane
Lawrence, Ernest O., Edwin McMillan and Malcolm C. Henderson—No. 7
—— see McMillan
Loeb, L. B.—see Cravath
Loughridge, D. H.—see Young

MacPherson, H. G.—No. 9
McMillan, Edwin and Ernest O. Lawrence—No. 6
—— see Lawrence
More, Kenneth R.—No. 17
Munier, John H.—see Delsasso

Obert, Leonard—see Knudsen

Posin, D. Q.—No. 28

Richardson, J. R. and Franz N. D. Kurie—No. 4
Ridenour, L. N., D. M. Yost and K. Shinohara—No. 1
Rose, John E.—see Henderson

Shinohara, K.—see Ridenour
Smith, Sinclair—No. 22
Stephens, W. E.—No. 11
Strait, L. A.—see Jenkins
Strong, John and E. Gaviola—No. 20
—— see Brice

Varney, Robert N.—No. 10

White, H. E.—see Ballard

Yost, D. M.—see Ridenour
Young, R. W. and D. H. Loughridge—No. 31

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CONTENTS

PHYS. REV. 45 (1934) FEBRUARY 1

Azimuthal Longitudinal Effect in Cosmic Rays . . . . . ROBERT A. MILLIKAN AND H. VICTOR NEHER 205

Modification of Prins' Formula for Diffraction of X-Rays by a Perfect Crystal . . . . . FRANKLIN MILLER, JR. 209

Band Spectrum of Beryllium Hydride at 10,000A . . . WILLIAM W. WATSON 213

Ultraviolet Absorption Band of I_2. JOHN E. VANCE AND JOHN R. HUFFMAN 215

On the Redward Shift of Spectral Lines of Nebulae . . . . P. I. WOLD 217

Temperature Variation Method to Assist in Vibrational Analyses of Complex Molecular Spectra . . . . . J. H. CLEMENTS 220

Ultraviolet Absorption Spectrum of Sulphur Dioxide . . . . J. H. CLEMENTS 224

Spectra of Lead IV and Bismuth V . . . . . G. K. SCHOEPFLE 232

Vibrations of Symmetrical Tetratomic Molecules . . JESSE E. ROSENTHAL 235

Periodicity of Mayer's Function . . . . . C. H. DOUGLAS CLARK 238

Accommodation Coefficient of Mercury Ions on a Mercury Surface . . . . . R. C. MASON 241

Letters to the Editor:

On the Nuclear Radius . . . . . ARTHUR K. SOLOMON 249

Evidence of the Hardening of Cosmic Rays in Passing through Matter . . . . . W. F. G. SWANN 250

Theoretical Limit of the Transmission of Solar Radiation by the Earth's Atmosphere in the Red Spectral . . . . . ARTHUR ADEL AND V. M. SLIPHER 251

On the Band Spectrum of Sulfur . . . . . ARTHUR CROMPTON 251

Isotopes in Induced Radioactivity . . . T. R. WILKINS AND L. S. SKINNER 251

Raman Effect of Water Vapor . . . . . DAVID BERGER 252

Proceedings of the American Physical Society:

LOS ANGELES MEETING, December 31-32, 1934; Minutes and Abstracts 1-30; Author Index 253

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